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THE EFFECT OF KEY PROCESS VARIATIONS UPON THE MAGNETIC PROPERTIES OF HDDR (Pr,Dy)-(FE,Co)-B-Nb BONDED MAGNETS.

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The effects of processing parameters upon the magnetic properties of (Pr,Dy)-(Fe,Co)-B-(Nb/Zr) type permanent magnets prepared from a Hydrogenation, Disproportionation, Desorption and Recombination (HDDR) treatment have been investigated. In particular, the state of the precursor material (as-cast and annealed), the hydrogenation pressure and alloy additions (Dy, Nb and Zr) were studied. Higher initial hydrogen pressures (pH_2>0.15 MPa) were found to be necessary to obtain high magnetic properties from Dy-containing HDDR powder compositions. The addition of dysprosium to Nb-containing magnets resulted in an increase in $_iH_c$ from 613±10 kAm^{-1} to around 1000±20 kAm^{-1} for the particular processing conditions.

1 Introduction

The Hydrogenation, Disproportionation, Desorption and Recombination (HDDR) process is an alternative technique to melt quenching route for the production of highly coercive NdFeB magnetic powder.[1-4] This gas-solid reaction transforms the relatively coarse grain structure of the starting material to a sub-micrometer grain structure by subjecting the NdFeB alloy to a hydrogen and then vacuum atmosphere at elevated temperatures. When the neodymium component is substituted with praseodymium in the alloy composition, the magnetic properties of this HDDR powder can be inferior to those of Nd-based materials.[5] However, a Pr-(Fe,Co)-B-Ga-Zr powder has been reported to have high remanence and low coercivity following an HDDR treatment.[6] More recently, it has been shown that an annealed $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6M_{0.1}$ (M=Zr or Nb) alloy when subjected to a straightforward HDDR treatment (pH_2 = 0.1 MPa) can be produce a magnetically anisotropic powder with exceptionally high remanence (B_r ~1000 mT) and reasonable coercivity ($_iH_c$ ~790 kAm^{-1}) in a preferred orientation.[7-10] In a further study which used these HDDR parameters (including pH_2 = 0.1 MPa)[9] the influence of Dy and Ga additions were observed to deteriorate the magnetic properties (B_r=498 mT, $_iH_c$=200 kAm^{-1}) of Pr-(Fe,Co)-B based HDDR magnets.[9] This current study has returned to these compositions and employed a range of different HDDR processing parameters with a view to optimizing the magnet properties of the resultant HDDR powder. Dy and Nb-free magnets together with Zr containing HDDR compositions were also studied for comparison.

2 Experimental Procedure

Alloy compositions were prepared in both the as-cast and annealed (1100°C for 20 hours) conditions as detailed in Table I. Material from each type of precursor was crushed into coarse particles and 9 g batches were placed in an HDDR reactor. The reactor was evacuated to a pressure of ~10^{-1} mbar and hydrogen was introduced to a pressure of pH_2 (where pH_2 ranged between 0.08 and 0.25 MPa). Hydrogen was initially introduced to the reactor at room temperature to facilitate the decrepitation of the precursor material and aid reaction uniformity. The temperature of the reactor was then raised to 100°C and held for 30 minutes. Subsequent heating brought the reactor

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up to 770°C at 15°C/min and then to 860°C at a slower rate of 5°C/min. At this point the disproportionation reaction was enabled for a 15-minute period.[8] Desorption and recombination then occurred with the application of a vacuum at 860°C. Some ten minutes later, when the pressure had reached 10^{-1} mbar the recombination stage was assumed to have reached completion, the furnace was removed and the reactor was rapidly cooled with a water-cooled copper jacket.

The resultant material was crushed in air to a particle size of <74 µm. This fine powder from each composition was then encapsulated within a cylindrical rubber bags (Ø=0.9 cm, l=1.3 cm), pulsed magnetized in a 6.0 T field and isostatically pressed at 200 MPa. These green compacts were then consolidated with molten wax, which infiltrate the porous matrix between compressed HDDR powder particles in the bags. The mixture was then cooled to room temperature and the excess wax was removed to form a cylindrical magnet.

Magnet samples were characterized with second-quadrant demagnetization curves with a permeameter. Remanence values were normalized to assume 100% density for the HDDR wax-bonded sample, and on the assumption that the density and remanence have a linear relationship.

The powder morphology of samples was characterized with a scanning electron microscope.

The degree of particle alignment achieved in magnets achieved with this isostatic press technique is currently under investigation using an X-ray diffraction technique and will be reported in the near future.

TABLE I: Details of compositions investigated.

Composition	Conditions of alloy investigated	Nature of investigation
$Pr_{13.8}Fe_{63.5}Co_{16.7}B_6$	As-cast and annealed	Magnetic Properties Degree of Anisotropy
$Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$	As-cast and annealed	HDDR Treatment Parameters Magnetic Properties Degree of Anisotropy Particle Morphology
$Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$	As-cast and annealed	HDDR Treatment Parameters Magnetic Properties Degree of Anisotropy Particle Morphology
$Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$	As-cast and annealed	Magnetic Properties Degree of Anisotropy

3 Results and Discussion

The variation in magnetic properties of HDDR magnets produced from an annealed $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ composition and over a range of hydrogenation pressures is illustrated in Figure 1. Overall, high magnetic properties were achieved with samples prepared using an initial hydrogen pressure of $p(H_2)$ = 0.093 MPa. Higher hydrogen pressures produced magnets with considerable coercivity but lower remanence. This is consistent with data from a previous study,[9] where it was shown that highly anisotropic $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ wax-bonded magnets could be produced using an initial hydrogen pressure of 0.1 MPa and a batch size of 13 g. Figure 2 details the variation in B_r and $_iH_c$ for dysprosium containing HDDR magnets, which were prepared from annealed $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ and treated with a range of $p(H_2)$ levels. This dysprosium containing material exhibited a need for higher initial hydrogen pressures ($p(H_2)$ = 0.12 MPa) to produce high magnetic properties. The presence of 1.0 at.% dysprosium yielded in an increase in the intrinsic coercivity, but as expected, it also caused a decrease in remanence.

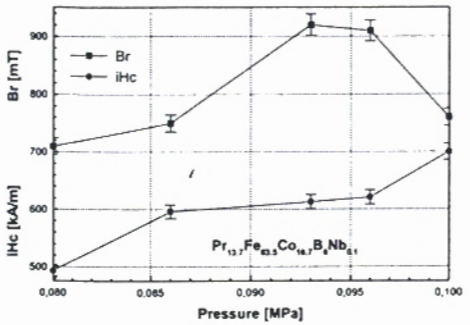

Figure 1. Magnetic properties of $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR wax-bonded magnets produced with different hydrogen pressure.

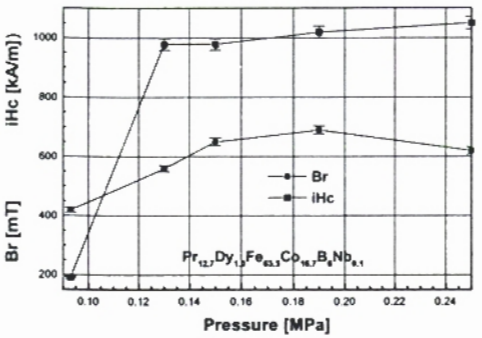

Figure 2. Magnetic properties of $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$HDDR wax-bonded magnets produced with different hydrogen pressure.

A comparison of hydrogen pressure as a function of process time, for both compositions during the HDDR treatment is plotted in Figure 3. At low temperatures, the Dy-containing alloy appears to absorb more hydrogen than the Dy-free alloy. Conversely, at high temperatures, the $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ alloy absorbs less hydrogen, indicating that the reaction during the HDDR treatment was incomplete for this alloy composition. At an initial hydrogen pressure of $p(H_2)$= 0.19 MPa, the absorption behavior of this alloy, during the present HDDR treatment, was similar to that of the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ alloy (shown in Figure 3).

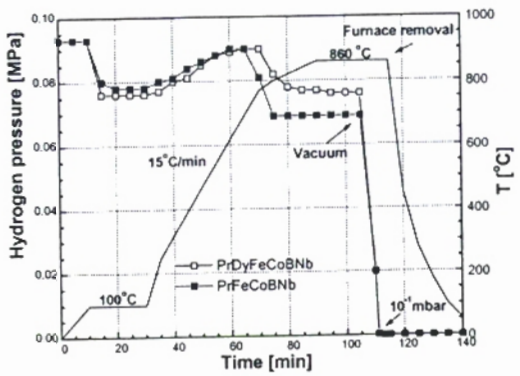

Figure 3. Schematic of hydrogen pressure and temperature profile for the HDDR process of compositions with and without Dy.

The effect of a Nb addition upon the magnetic properties of the HDDR magnets is shown in Table II. The highest remanence (920 mT) was observed in a Nb-containing magnet, which was prepared from an aligned HDDR powder and an annealed precursor material. In fact it is worth noting that the Nb addition consistently improved B_r values for all of these HDDR magnets. The highest intrinsic coercivity (670 kAm^{-1}) was achieved in a Nb-free isotropic magnet (prepared using a non-aligned powder). Isotropic magnets prepared using a Dy-free alloy in the annealed state demonstrated lower remanences than those exhibited by aligned magnets of the same alloy, but with an as-cast precursor. The effect of Nb and Zr additions upon the magnetic properties of Dy-containing HDDR magnets is detailed in Table III. As in the previous case, the highest remanence (660 mT) was achieved with the Nb and Zr-containing aligned magnets prepared from annealed alloy precursors. The highest intrinsic coercivity (1030 kA/m) was attained from the Nb-containing magnets. In contrast with the previous case, isotropic magnets prepared using the annealed Dy-containing alloy show higher remanences than those of aligned magnets produced with the same alloy in the as-cast condition.

The effect of using different amounts of precursor material in the HDDR reactor upon the magnetic properties of aligned $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR magnets is shown in Table IV. A progressive increase in remanence, and presumably anisotropy, is observed with increasing batch sizes. The coercivity is also seen to increase in magnets from sample batches up to 9 grams and then decrease thereafter. The sensitivity of the magnetic properties upon the batch size is strongly dependent upon the exothermic and endothermic nature of the gas-solid reaction, and hence the particular size and configuration of the apparatus employed.

TABLE II: Magnetic properties of $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_x$ HDDR magnets (X= 0, 0.1) prepared using an initial hydrogen pressure of 0.093 MPa and measured in a permeameter (error:± 2%).

Precursor Alloy Condition	Nb (at%)	B_r (mT)	$_iH_c$ (kAm^{-1})	$_bH_c$ (kAm^{-1})	$(BH)_{max}$ (kJm^{-3})	SF=$H_k/_iH_c$
Annealed	0	840	660	460	96	0.39
Aligned	0.1	920	613	454	106	0.43
Annealed	0	560	670	350	48	0.33
Isotropic	0.1	600	653	334	50	0.31
As-cast	0	640	540	334	55	0.32
Aligned	0.1	660	549	326	54	0.30

TABLE III: Magnetic properties of $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6M_{0.1}$ HDDR magnets (M= Nb, Zr) prepared using an initial hydrogen pressure of 0.22 MPa and measured in a permeameter (error:± 2%).

Precursor Alloy Condition	Addition (0.1 at%)	B_r (mT)	$_iH_c$ (kAm^{-1})	$_bH_c$ (kAm^{-1})	$(BH)_{max}$ (kJm^{-3})	SF=$H_k/_iH_c$
Annealed	Nb	660	1030	450	75	0.36
Aligned	Zr	660	955	438	72	0.33
Annealed	Nb	570	995	366	52	0.22
Isotropic	Zr	620	995	430	72	0.30
As-cast	Nb	510	846	302	38	0.19
Aligned	Zr	540	676	287	39	0.18

TABLE IV: Magnetic properties of $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR magnets prepared using batches of various weights (initial hydrogen pressure of 0.093 MPa) and measured in a permeameter (error:± 2%).

Weight	B_r (mT)	$_iH_c$ (kAm^{-1})	$_bH_c$ (kAm^{-1})	$(BH)_{max}$ (kJm^{-3})	SF=$H_k/_iH_c$
6.0	740	462	326	60	0.31
8.0	850	581	398	81	0.40
9.0	920	613	454	106	0.43
11.0	940	533	366	87	0.33

Figure 4 shows a back-scattered electron image of the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR powder (magnet properties: B_r= 920 mT and $_iH_c$= 613 kAm^{-1}) obtained from a process with an initial hydrogen pressure of 0.093 MPa. A uniform distribution of grains with diameters between 300 and 800 nm can be observed. No abnormal grain growth is evident. Figure 5 shows a back-scattered electron image of the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR powder (magnet properties: B_r= 680 mT and $_iH_c$= 676 kAm^{-1}) obtained at an initial hydrogen pressure of 0.15 MPa. A number of grains with diameters >1 μm were observed in this HDDR powder. Thus, it can be summated that higher hydrogenation pressures promote grain growth during HDDR processing of Dy-free alloy compositions, and this is evident from the decrease in remanence and increase in coercivity (Figure 1). Hence, processing $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ material at higher hydrogen pressures appears to reduce the anisotropic nature of this HDDR powder.

Figure 6 shows a back-scattered electron image of the $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR powder (magnet properties: B_r= 650 mT and $_iH_c$= 980 kAm^{-1}) obtained at a hydrogen pressure of 0.15 MPa. Grains with diameters >2 μm can be seen in this HDDR material. The higher coercivity of this magnet can also be attributed to the Dy addition. Further microstructural studies are underway in an attempt to explain the magnetic behavior observed in this work. X-ray diffraction studies are in progress to determine the degree of magnetic alignment as a function of the of HDDR sample batch size.

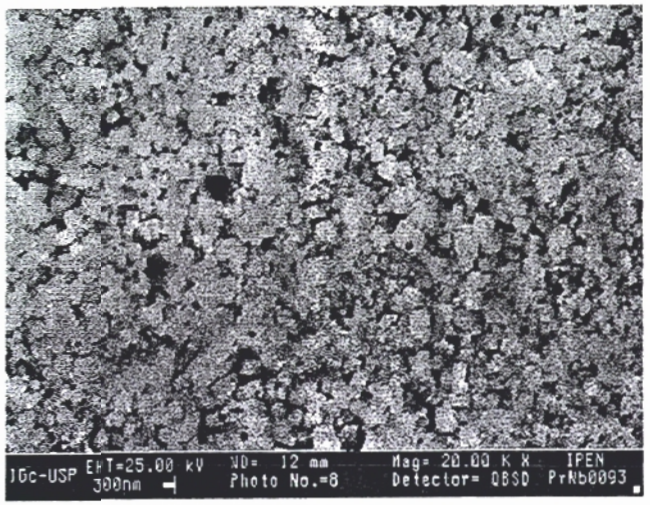

Figure 4. Back-scattered electron image of $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR powder processed at initial H_2 pressure of 0.09 MPa.

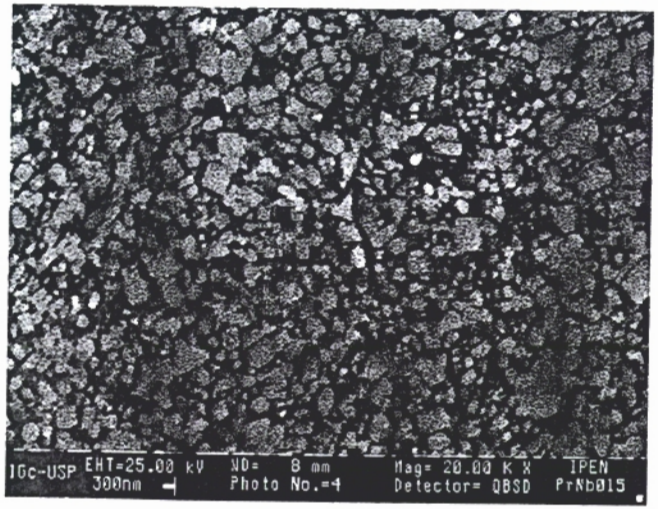

Figure 5. Back-scattered electron image of $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR powder processed at initial H_2 pressure of 0.15 MPa.

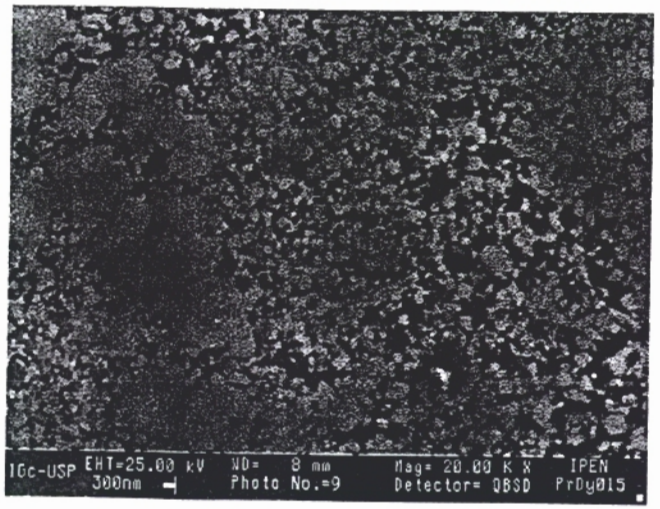

Figure 6. Back-scattered electron image of $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR powder processed at initial H_2 pressure of 0.15 MPa.

4 Conclusions

- Data obtained in this study illustrates the importance of the hydrogenation pressure for producing highly coercive HDDR magnets ($_iH_c$>1000 kAm^{-1}) from a $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ composition.

- At the appropriate hydrogen pressure (>0.2 MPa), both alloys (with and without Dy) absorbed the same amount of hydrogen during the HDDR treatment, and hence both types of precursor material can undergo a complete HDDR reaction.
- HDDR magnets from the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ annealed alloy precursor exhibited highly anisotropic magnetic properties (B_r/M_s>0.5), whereas the equivalent $Pr_{12.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR magnets yielded more isotropic magnetic properties with higher intrinsic coercivities.
- A Zr addition was observed to improve the magnetic properties of isotropic PrDyFeCo-based magnets.
- An annealed precursor material generally yields a greater degree of anisotropy in the magnetic properties of HDDR magnets.

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