MAGNETIC PROPERTIES OF PR-FE-CO-B BONDED HDDR MAGNETS WITH ALLOYING ADDITIONS

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ABSTRACT

This paper reports the results of investigations of the microstructures and magnetic properties of Pr-Fe-Co-B bonded magnets represented by the formulae, $Pr_{14}Fe_{63.9}Co_{16}B_6M_{0.1}$ (M = Ti, V, Cr, Ni, Zr, Nb or Mo), $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}T_{0.1}$ (T = Al, Si, P, Cu or Ga) and $Pr_{14}Fe_{63.6}Co_{16}B_6Nb_{0.1}R_{0.3}$ (R = Gd, Tb or Dy). The effects of additions on the magnetic properties of PrFeCoB-based magnets have been studied. Magnetically hard powders have been produced from homogenised alloys using the hydrogenation, disproportionation, desorption and recombination (HDDR) process. The HDDR powders were isostatically pressed and bonded with cyanoacrylate adhesive to form permanent magnets.

Keywords: Pr-based alloys; magnetic materials; hydrides; magnetic properties; PACS: 71.20.Eh

INTRODUCTION

Neodymium- and praseodymium-based bonded magnets can be successfully prepared by the HDDR process (see for instance, Ref. [1-17] or review [18]). Isotropic magnets are prepared using the basic alloy without additions and anisotropic with the additions of cobalt, gallioum, zirconium and niobium. In the past, vanadium, chromium, aluminium have only been added to neodymium based bonded HDDR magnets [19]. In the present work, a further study has been carried out on these materials with various additions (Al, Si, P, Ti, V, Cr, Ni, Cu, Ga, Zr, Nb, Mo, Gd, Tb or Dy). A $Pr_{14}Fe_{64}Co_{16}B_6$ alloy has been used as the base alloy for the additions

and included in this study as a standard reference. A standard HDDR process appropriated for praseodymium-based bonded magnets [11] has also been used in the present work.

It is well established that each particular composition requires its own set of processing parameters as the thermodynamic stability and microstructure of the parent compound is modified in a specific manner by the addition of a certain element. It is also known that anisotropy can be achieved by appropriate processing and for 2-14-1 compounds, without the addition of dopants. It has been reported that to process $Pr_{13.7}Dy_{1.0}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ HDDR magnets with good magnetic properties, higher hydrogen pressure is necessary than that used for processing Dy-free magnets [17]. A number of variables affect the HDDR process [31] and, therefore, it is easier to use processing conditions that have yielded good results in the past and then seek the dopant that imparts the best magnetic properties. The HDDR treatment used in this investigation for the Pr-based alloys is very convenient because it uses a moderate temperature, a relatively low hydrogen pressure and rapid cooling rate. For the present processing conditions, that uses a straightforward HDDR treatment, finding an element that induces high anisotropy or high coercivity was considered to be very important.

EXPERIMENTAL PROCEDURE

Various commercial alloys were investigated after a homogenization treatment in vacuum at 1100^oC for 20 h. The chemical analyses of the as-cast alloys are given in Table 1. As per the supplier's specification, the alloys contain neodymium (0.2~0.7 wt %), aluminium (0.02~0.2 wt %) and silicon (0.01~0.04 wt %) as an impurity. The analysed amount of phosphorous in the $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}P_{0.1}$ alloy is much less than that specified in the formula. According to the supplier the added phosphorous would not go into solution to any significant degree and instead formed an insoluble phosphate slag on the melt surface. Hence, the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.1}$ alloy does contain some phosphorous, but at somewhat lower level (~0.01wt%) than that suggested by the nominal composition (0.05wt%).

The following procedure was adopted to produce the Pr-based bonded magnets via the HDDR process [11-20]. The annealed alloys were crushed into coarse lumps and 8 g batches were placed in the HDDR reactor. This reactor was

then evacuated to the backing-pump pressure ($\sim 10^{-1}$ mbar) and hydrogen introduced until the pressure of 0.097 MPa. The temperature of the reactor was held at 100°C for 30 minutes to provide sufficient time for the hydrogen decrepitation (HD) reaction to go to completion. The reactor was then heated to 770 ^{o}C at 15 ^{o}C/min and further up to the desorption temperature (860 ^{o}C) at 5°C/min, with a dwell time of 15 min prior to desorption [11]. Subsequent desorption and recombination was carried out under vacuum at the same temperature until a pressure of 10^{-1} mbar was achieved (<10 min). Rapid cooling of the material was carried out by removing the furnace from the HDDR reactor and by coupling a water-cooled copper coil to the reactor tube. The resultant powder was crushed in air until all the material passed through a < 75 m sieve. The fine powder was subsequently encapsulated in a small cylindrical rubber bag, pulsed in a magnetic field of 6 T and pressed isostatically at 200 MPa (isotropic magnets were pressed without pulsing). The resultant green compacts were consolidated by immersion (vacuum impregnated) in cyanoacrylate adhesive with a low viscosity (3 Pa s) and heating to 70°C. The bonded sample was then allowed to cool to room temperature and the excess material removed to yield a cylindrical magnet (= 5.0±0.3 g cm^{-3}). Magnetic characterization of the HDDR magnets was carried out using a permeameter (accuracy: 2%). Measurements were performed after saturation in a pulsed field of 6 T. Remanence values have been normalized assuming 100% density (7.5 g cm^{-3}) for the HDDR sample and by also considering a linear relationship between density and remanence.

Previously Pr-based HDDR magnets prepared in our laboratory used an isostatic press and paraffin as the bonding agent. In this work cyanoacrylate adhesive has been used with no significant difference (less than the measurement error) in the magnetic properties but with considerable improvement in the mechanical resistance of the samples (isostatically pressed and paraffin or wax or bonded magnets cannot withstand more than two demagnetisations in the permeameter without loosing integrity).

RESULTS AND DISCUSSION

Figures 1 shows the percentage variation on the remanence of the PrFeCoBM-based HDDR bonded magnets as a function of the atomic number (Z) of the addition element. These percentage variations were calculated taking the

remanence (0.59 T) of an isotropic $Pr_{14}Fe_{bal}Co_{16}B_6$ magnet as a reference. In general, with exception of dysprosium, all elements added to the base alloy induced some anisotropy in these Pr-based HDDR materials. Surprisingly good results were obtained with the addition of phosphorous and aluminium to the magnetic alloys. Copper was less effective in inducing anisotropy in these Pr-Fe-Co-B-type bonded magnets. Under the present processing condition, dysprosium addition to the bonded HDDR magnets led to a dramatic reduction on the remanence. It has been reported that for successfully processing Pr-Fe-Co-B-based alloys containing this metal a higher hydrogen pressure is necessary [17].
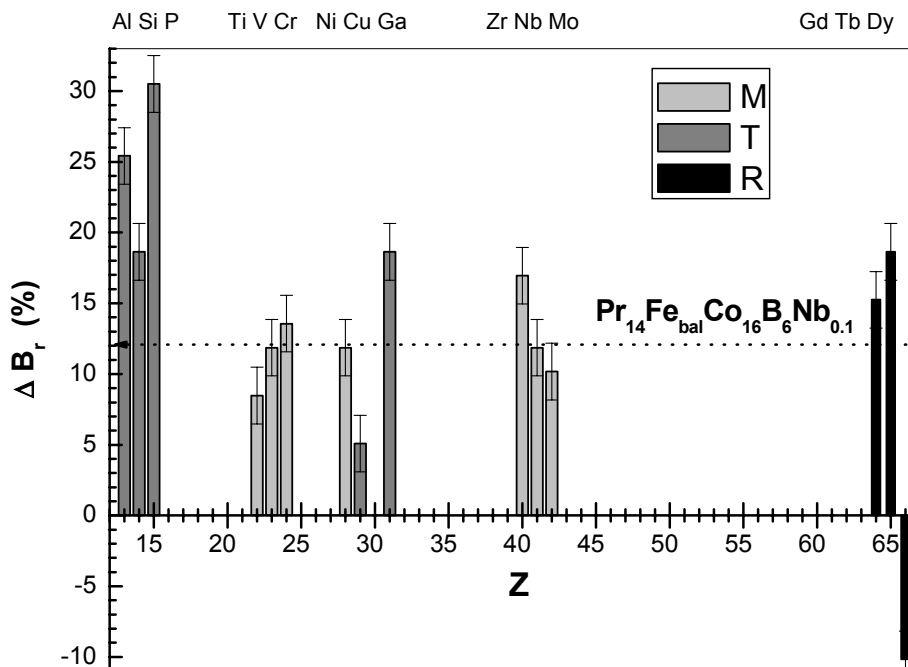

Figura. 1. Remanence of the $Pr_{14}Fe_{63.9}Co_{16}B_6M_{0.1}$, $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}T_{0.1}$ and $Pr_{14}Fe_{63.6}Co_{16}B_6Nb_{0.1}R_{0.3}$ HDDR bonded magnets plotted against the atomic number of the addition element.

Figure 2 shows the percentage variation on the intrinsic coercivity of the PrFeCoBM-based HDDR bonded magnets as a function of the atomic number of the addition element. These percentage variations were calculated taking the intrinsic coercivity (0.94 T) of an isotropic $Pr_{14}Fe_{bal}Co_{16}B_6$ magnet as a reference. In contrast to the remanence behaviour, mixed results were obtained with this magnetic

property. Very good results were obtained with the addition of vanadium and nickel to the bonded HDDR magnets. Good results were obtained with zirconium and niobium.
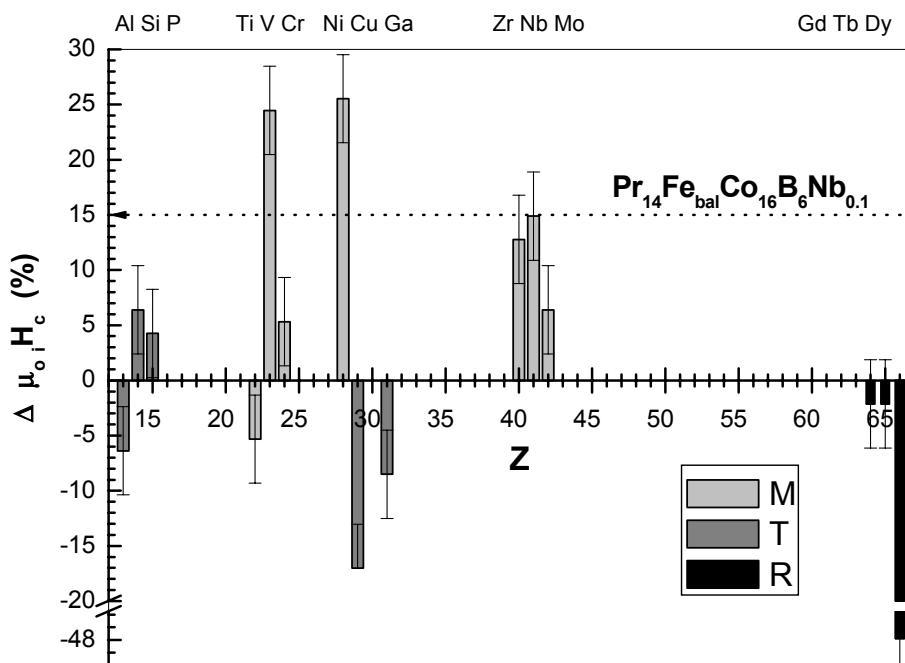

Figure. 2. Intrinsic coercivity of the $Pr_{14}Fe_{63.9}Co_{16}B_6M_{0.1}$, $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}T_{0.1}$ and $Pr_{14}Fe_{63.6}Co_{16}B_6Nb_{0.1}R_{0.3}$ HDDR bonded magnets plotted against the atomic number of the addition element.

Aluminium, titanium and gallium addition reduced somewhat the intrinsic coercivity of these Pr-based HDDR magnets. Copper and dysprosium additions were deleterious to this magnetic property. Under the present processing condition dysprosium addition to the bonded HDDR magnets caused a dramatic reduction on the coercivity. As mentioned previously, it has been reported [17] that a higher processing hydrogen pressure is necessary for obtaining high intrinsic coercivity in Pr-Fe-Co-B-Dy-based bonded magnets and this also could be the case for the Al, Ti, Cu, Ga, Gd and Tb. Further investigations are presently underway to verify this possibility. Table 2 summarizes the magnetic properties of the praseodymium-based bonded magnets prepared using the HDDR powder and cyanoacrylate adhesive. Further microstructural studies and texture analysis (x-ray) on all the starting alloys, and corresponding HDDR powders, are underway and the results will be presented and discussed in detail in a forthcoming paper.

Table 1 Composition of the as-cast praseodymium-based alloys.

Nominal composition (at %)	Analyzed composition (wt%)					
	Pr[*]	Fe	Co	B	Nb	M/T
$Pr_{14}Fe_{bal}Co_{16}B_6$	30.01	54.56	14.31	1.01	---	---
$Pr_{14}Fe_{bal}Co_{16}B_6Ti_{0.1}$	29.83	54.76	14.25	0.98	---	0.07
$Pr_{14}Fe_{bal}Co_{16}B_6V_{0.1}$	30.09	54.37	14.40	1.01	---	0.06
$Pr_{14}Fe_{bal}Co_{16}B_6Cr_{0.1}$	30.29	54.08	14.44	0.96	---	0.08
$Pr_{14}Fe_{bal}Co_{16}B_6Ni_{0.1}$	30.08	54.40	14.35	1.00	---	0.11
$Pr_{14}Fe_{bal}Co_{16}B_6Zr_{0.1}$	30.06	54.32	14.42	1.01	---	0.11
$Pr_{14}Fe_{bal}Co_{16}B_6Mo_{0.1}$	30.35	53.89	14.51	1.00	---	0.16
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$	30.35	54.11	14.34	0.96	---	0.14
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}$	30.33	54.18	14.24	0.99	0.18	0.02
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Si_{0.1}$	30.07	54.36	14.14	1.00	0.16	0.07
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.1}$	30.49	53.86	14.33	1.02	0.13	0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Cu_{0.1}$	30.51	53.79	14.25	0.99	0.15	0.13
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Ga_{0.1}$	30.44	53.85	14.28	1.00	0.14	0.11
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Gd_{0.3}$	29.65	54.22	14.22	1.02	0.14	0.69
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Tb_{0.3}$	29.94	54.05	14.16	0.98	0.12	0.71
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Dy_{0.3}$	29.61	54.33	14.23	0.97	0.14	0.65

(* Pr + ~0.3wt%Nd)

Table 2 Remanence and coercivity of $Pr_{14}Fe_{63.9}Co_{16}B_6M_{0.1}$, $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}T_{0.1}$ and $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}R_{0.3}$ HDDR bonded magnets.

Composition	B_r (T)	ΔB_r (%)	$\mu_o {}_iH_c$ (T)	$\Delta\mu_o {}_iH_c$ (%)
$Pr_{14}Fe_{bal}Co_{16}B_6$ (isotropic)	0.59±0.01	---	0.94±0.02	---
$Pr_{14}Fe_{bal}Co_{16}B_6Ti_{0.1}$	0.64±0.01	8.47±2	0.89±0.02	-5.32±4
$Pr_{14}Fe_{bal}Co_{16}B_6V_{0.1}$	0.66±0.01	11.86±2	1.17±0.02	24.47±4
$Pr_{14}Fe_{bal}Co_{16}B_6Cr_{0.1}$	0.67±0.01	13.56±2	0.99±0.02	5.32±4
$Pr_{14}Fe_{bal}Co_{16}B_6Ni_{0.1}$	0.66±0.01	11.86±2	1.18±0.02	25.53±4
$Pr_{14}Fe_{bal}Co_{16}B_6Zr_{0.1}$	0.69±0.01	16.95±2	1.06±0.02	12.77±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$	0.66±0.01	11.86±2	1.08±0.02	14.89±4
$Pr_{14}Fe_{bal}Co_{16}B_6Mo_{0.1}$	0.65±0.01	10.17±2	1.00±0.02	6.38±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}$	0.74±0.01	25.42±2	0.88±0.02	-6.38±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Si_{0.1}$	0.70±0.01	18.64±2	1.00±0.02	6.38±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.1}$	0.77±0.01	30.51±2	0.98±0.02	4.26±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Cu_{0.1}$	0.62±0.01	5.08±2	0.78±0.02	-17.02±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Ga_{0.1}$	0.70±0.01	18.64±2	0.86±0.02	-8.51±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Gd_{0.3}$	0.68±0.01	15.25±2	0.92±0.02	-2.13±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Tb_{0.3}$	0.70±0.01	18.64±2	0.92±0.02	-2.13±4
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Dy_{0.3}$	0.53±0.01	-10.17±2	0.49±0.01	-47.87±4

$\Delta B_r = [(Br/0.59)-1]100$; $\Delta\mu_o {}_iH_c = [(Br/0.94)-1]100$

CONCLUSIONS

It has been shown that vanadium, nickel, zirconium and niobium are a good choice for a single addition to $Pr_{14}Fe_{bal}Co_{16}B_6$ HDDR bonded magnets. Niobium and zirconium induce considerably anisotropy whereas vanadium and nickel enhance the intrinsic coercivity. It has also been shown that when the second element (Al, Si, P, Cu or Ga) is added to the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$ alloy only phosphorous and aluminium cause the significant increase in remanence. Under the present processing conditions rare earth addition (Gd, Tb or Dy) to the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$ alloy showed no beneficial effect to the magnetic properties of the bonded magnets

ACKNOWLEDGEMENTS

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