

## The Influence of Si, Ga and Gd Content on the Magnetic Properties of Pr-Fe-Co-B-Nb HDDR Bonded Magnets

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**Abstract:** This paper reports the results of investigations carried out to determine the microstructure and magnetic properties of some praseodymium-based magnets represented by the formula  $\text{Pr}_{14}\text{Fe}_{63.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{M}_x$ . Bonded magnets were prepared the annealed 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. The effect of addition element content on the magnetic properties of these magnets was investigated. The amount of addition has a significant effect on the magnetic behaviour of these bonded magnets.

### Introduction

Bonded magnet powders prepared by the hydrogenation, disproportionation, desorption and recombination (HDDR) process are high coercivity materials and these can be obtained by exposing rare earth-based alloys to hydrogen at elevated temperatures (examples in [1-10]). Bonded praseodymium-based HDDR magnets are easier to produce with a relatively straight forward HDDR treatment [11-17]. It has also been shown that a number of additions can influence considerably the magnetic properties of the praseodymium based HDDR bonded magnets. The influence of cobalt, praseodymium, niobium and boron content on the Pr-Fe-Co-B-Nb-based HDDR magnets have been investigated [18-21]. This paper reports the results of a complementary work carried out on  $\text{Pr}_{14}\text{Fe}_{63.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{M}_x$  (M= Ga, Si or Gd;  $x = 0-0.5$ ). This investigation was undertaken to optimize the addition content with respect to the magnetic properties of the HDDR magnets.

### Experimental Procedure

Various commercial alloys in the homogenized state were studied. The chemical analyses of the as-cast alloys are given in Table 1. As per the supplier's specification, the alloys contain neodymium (~0.3 wt %), aluminium (~0.1 wt %) and silicon (~0.03 wt %) as an impurity. Homogenization treatment was carried out in vacuum at 1100°C for 20 h. The following procedure was adopted to produce the Pr-based bonded magnets via the HDDR process [11-16]. 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 °C at 15

°C/min and further up to the desorption temperature (860 °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  $< 75 \mu\text{m}$  sieve. The fine powder was subsequently encapsulated in a small cylindrical rubber bag, pulsed in a magnetic field of 6.0 T and pressed isostatically at 200 MPa (isotropic magnets were prepared without pulsing). The resultant green compacts were consolidated by immersion in cyanoacrylate adhesive (viscosity: 3 Pa s) and heating to 70°C (vacuum was necessary to enable the liquid adhesive to penetrate the HDDR powder compact). The bonded sample was then allowed to cool to room temperature and the excess material removed to yield a cylindrical magnet ( $\rho=5.0\pm0.3 \text{ g cm}^{-3}$ ). Magnetic characterization of the HDDR magnets was carried out using a permeameter (accuracy: 2%). Measurements were performed after saturation in a pulsed field of 6.0 T. Remanence values have been normalized assuming 100% density ( $7.5 \text{ g cm}^{-3}$ ) 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) bonded magnets cannot withstand more than two or three demagnetisations in the permeameter without losing integrity. The microstructural examination of the HDDR material was carried out with the aid of a scanning electron microscope coupled to an EDX analysis facility.

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

Nominal composition (at%)	Analyzed composition (wt%)						
	Pr*	Fe	Co	B	Nb	Al	M
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	30.35	54.11	14.34	0.96	0.14	0.10	---
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Si}_{0.1}$	30.07	54.51	14.14	1.00	0.16	0.05	0.07
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Si}_{0.3}$	31.00	53.47	14.18	1.00	0.19	0.03	0.13
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Si}_{0.5}$	30.35	54.26	14.05	0.95	0.14	0.05	0.20
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.1}$	30.44	53.97	14.28	1.00	0.14	0.06	0.11
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.3}$	30.38	53.61	14.40	0.98	0.15	0.16	0.32
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$	30.54	53.58	14.23	1.01	0.15	0.03	0.46
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Gd}_{0.1}$	30.46	53.79	14.27	1.02	0.14	0.04	0.28
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Gd}_{0.3}$	29.65	54.20	14.22	1.02	0.16	0.06	0.69
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Gd}_{0.5}$	30.45	53.05	14.12	1.01	0.17	0.02	1.18

(\* Pr + ~0.3wt%Nd)

## Results and discussion

Variation in remanence and intrinsic coercivity of HDDR magnets, produced from homogenized alloys, as a function of silicon content is shown in Figure 1. Good remanence

( $B_r=0.69\pm0.01$  T) was achieved in the samples prepared from homogenized alloy without addition of silicon. A reasonable intrinsic coercivity ( $\mu_0 iH_c=1.06\pm0.02$  T) was also achieved in this reference HDDR magnet. A small addition of this element, up to 0.1 at%, improved slightly the remanence but decreased somewhat the intrinsic coercivity. Higher silicon contents produced a slight diminution on the remanence but a dramatic decrease in the intrinsic coercivity. Thus, under the present processing conditions this element is not beneficial to the magnetic properties of Pr-Fe-Co-B-Nb HDDR magnets.

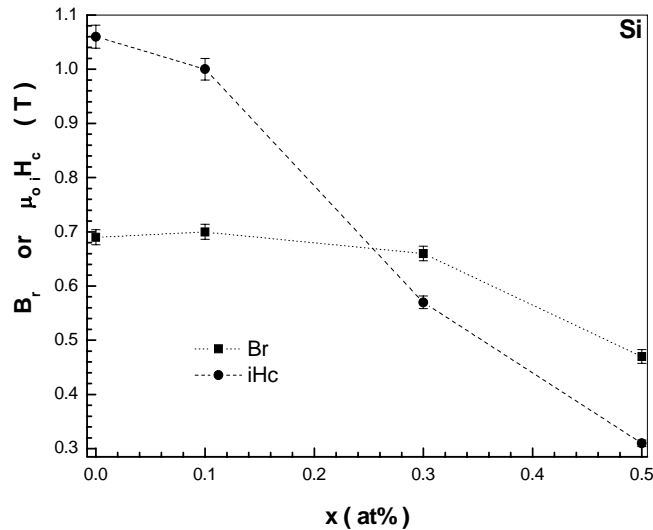


Fig. 1. Remanence and coercivity versus addition content for  $\text{Pr}_{14}\text{Fe}_{63.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Si}_x$  bonded magnets.

Variation in remanence and intrinsic coercivity of HDDR magnets, produced from homogenized alloys, as a function of gallium content is shown in Figure 2. A small addition of this element, up to 0.1 at%, also improved slightly the remanence but similar to the previous case, decreased somewhat the intrinsic coercivity. Higher silicon contents produced a slight diminution on the remanence. In the presence of 0.5 at% Ga, the intrinsic coercivity decreased from  $0.87\pm0.02$  T to  $0.70\pm0.02$  T. Thus, under the present processing conditions gallium addition is also detrimental to the magnetic properties of these Pr-based bonded magnets.

Variation in remanence and intrinsic coercivity of HDDR magnets as a function of gadolinium content is shown in Figure 3. Addition of this element, up to 0.5 at%, affected only slightly the remanence. The intrinsic coercivity was affected by this addition but not as severe to the silicon case. Again, under the present processing conditions gadolinium addition is also detrimental to the magnetic properties of these HDDR magnets. Table 2 summarizes the magnetic properties of the Pr-based bonded magnets prepared using the HDDR powder and cyanoacrylate adhesive.

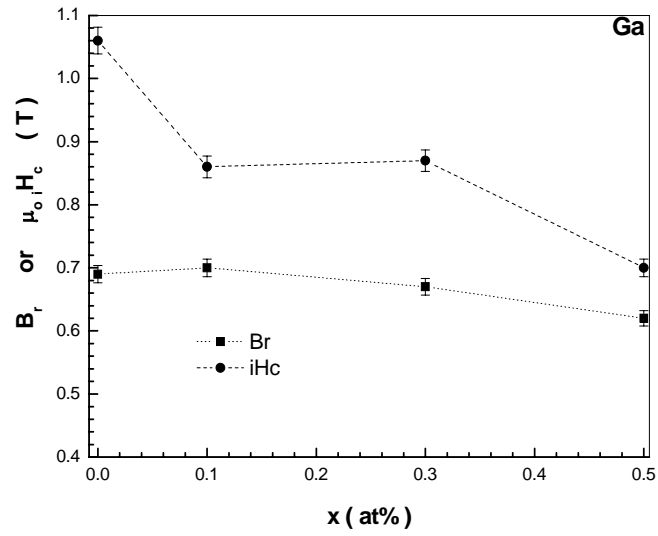


Fig. 2. Remanence and coercivity versus addition content for  $\text{Pr}_{14}\text{Fe}_{63.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_x$  bonded magnets.

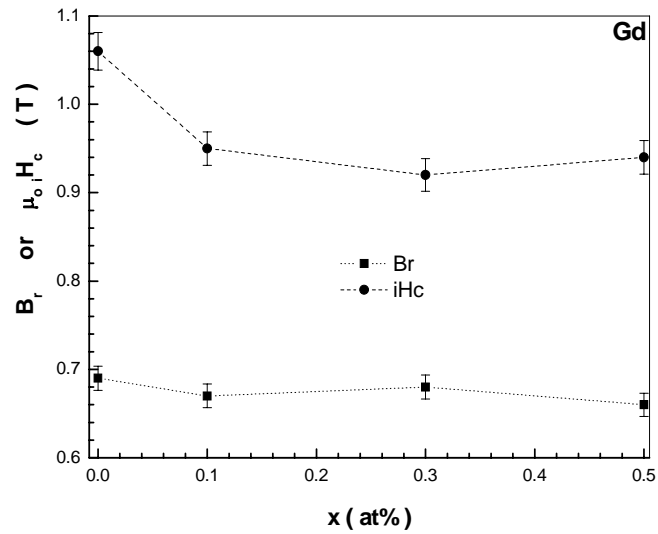


Fig. 3. Remanence and coercivity versus addition content for  $\text{Pr}_{14}\text{Fe}_{63.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Gd}_x$  bonded magnets.

Table 2 - Magnetic properties of  $\text{Pr}_{14}\text{Fe}_{63.9}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{M}_x$  HDDR bonded magnets.

Composition	$B_r$ (T)	$\mu_o i H_c$ (T)	$\mu_o b H_c$ (T)	$(BH)_{\max}$ (kJ/m <sup>3</sup> )	SF (ratio)
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	0.69±0.01	1.06±0.02	0.51±0.01	79.3±1.6	0.37±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Si}_{0.1}$	0.70±0.01	1.00±0.02	0.49±0.01	68.0±1.4	0.26±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Si}_{0.3}$	0.66±0.01	0.57±0.01	0.34±0.01	44.6±0.9	0.26±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Si}_{0.5}$	0.47±0.01	0.31±0.01	0.20±0.01	18.7±0.4	0.26±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.1}$	0.70±0.01	0.86±0.02	0.51±0.01	74.0±1.5	0.29±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.3}$	0.67±0.01	0.87±0.02	0.42±0.01	56.5±1.1	0.25±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$	0.62±0.01	0.70±0.02	0.38±0.01	46.9±1.1	0.26±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Gd}_{0.1}$	0.67±0.01	0.95±0.02	0.52±0.01	70.0±1.4	0.38±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Gd}_{0.3}$	0.68±0.01	0.92±0.02	0.46±0.01	62.9±1.3	0.27±0.01
$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Gd}_{0.5}$	0.66±0.01	0.94±0.02	0.50±0.01	65.3±1.3	0.32±0.01

## Conclusions

Under the present processing conditions, it has been shown that the addition of silicon, gallium and gadolinium to  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$  alloy is detrimental to the magnetic properties of the HDDR bonded permanent magnets. This is true in very low concentrations and particularly in higher contents of these elements. Silicon affected both, remanence and intrinsic coercivity whereas gallium and gadolinium influenced mostly the intrinsic coercivity. Good overall magnetic properties ( $B_r=0.69\pm0.01$  T;  $\mu_o i H_c=1.06\pm0.02$  T;  $\mu_o b H_c=0.51\pm0.01$  T;  $BH_{\max}=79.3\pm1.6$  kJm<sup>-3</sup>; SF=0.37±0.01) have been achieved for the HDDR  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$  magnets.

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## **The Influence of Si, Ga and Gd Content on the Magnetic Properties of Pr-Fe-Co-B-Nb HDDR Bonded Magnets**

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