

## The Effect of Niobium and Boron Content on Magnetic Properties and Corrosion Resistance of Pr-Fe-Co-B-Nb HD Magnets

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**Abstract:** The hydrogenation decrepitation process was employed to produce sintered magnets using a mixture of two alloys. The effect of niobium and boron content on the magnetic properties of Pr<sub>14</sub>Fe<sub>bal</sub>Co<sub>16</sub>B<sub>x</sub>Nb<sub>y</sub>-type sintered magnets was studied. Niobium and boron have a significant effect on the magnetic behavior of these permanent magnets. The optimum amount of boron was 6 at% and niobium should be kept below to 0.50 at%. The squareness factor (0.90) has been improved considerably and good overall magnetic properties ( $B_r=1320$  mT,  $iH_c=700$  kAm<sup>-1</sup> and  $(BH)_{max}=315$  kJm<sup>-3</sup>) have been achieved for the sintered magnets prepared from the Pr<sub>14</sub>Fe<sub>63.85</sub>Co<sub>16</sub>B<sub>6</sub>Nb<sub>0.15</sub> alloy.

### Introduction

Over many years, PrFeB-based sintered magnets with good magnetic properties have been produced with substitutions of Co, Al, Cu, Zr, Ga, Dy and Tb [1-8]. These magnets have been prepared using conventional powder metallurgy process [1-4], the hydrogen decrepitation (HD) process [5-7] and also by a combination of two alloys [8]. Recently, the influence of the cobalt content on the magnetic properties and corrosion resistance of PrFeCoCuNbB HD magnets has also been investigated [9]. Optimization of the boron and niobium contents with respect to magnetic properties of cobalt-containing Pr-based sintered magnets, however, has not been reported so far. This paper addresses this aspect and reports the results of further work carried out on Pr<sub>14</sub>Fe<sub>bal</sub>Co<sub>16</sub>B<sub>x</sub>Nb<sub>y</sub>-type HD sintered magnets ( $x = 4, 5, 6, 7$  and  $8$ ; and  $y = 0.0, 0.1, 0.15$  and  $0.5$ ) prepared from a mixture of cast alloys. Permanent magnets without additions (Pr<sub>14</sub>Fe<sub>80</sub>B<sub>6</sub> and Pr<sub>16</sub>Fe<sub>76</sub>B<sub>8</sub>) have been used as standard references in the present study.

### Experimental Procedure

Several commercial PrFeCoNbB alloys (14 at% Pr) in the annealed state (1100°C, 20 h) were used in this investigation. The chemical composition of the as-cast alloys are given in Table 1. As per the supplier's specification, the alloys contained neodymium (0.2~0.7 wt %), aluminium (0.02~0.2 wt %) and silicon (0.01~0.04 wt %) as impurities. The study of the Co-containing alloys and the details of the preparation of the HD sintered magnets have already been described in previous papers [8-10]. The Pr<sub>20.5</sub>Fe<sub>bal</sub>B<sub>5</sub>Cu<sub>2</sub> and Pr<sub>16</sub>Fe<sub>76</sub>B<sub>8</sub> alloys were not annealed prior to magnet processing.

In order to produce magnets from two alloys with distinct compositions [8] a praseodymium-enriched alloy (Pr<sub>20.5</sub>Fe<sub>bal</sub>B<sub>5</sub>Cu<sub>2</sub>), in the as cast condition, was used as sintering aid additive (16% in mass). Thus, the final composition of the sintered magnet is slightly richer in praseodymium (~15at % Pr) and contains a small amount of copper (~0.3 at% Cu). Hydrogenation of master and additive alloys (totalizing 15 g) was carried out simultaneously in a stainless steel vessel at a pressure of 1 bar and at 100°C. The decrepitated material was milled for 20 h using cyclohexane as the milling medium. The dried powder was then transferred to a small cylindrical rubber tube under nitrogen atmosphere. This powder was aligned by pulsing three times to a 6 T magnetic field, pressed isostatically at 1000 kg cm<sup>-2</sup> and then vacuum sintered for 1 h at 1030 °C,

followed by cooling inside the furnace. To evaluate the effect of additions only on sintering, no post-sintering heat treatment was carried out. Magnetic measurements of the HD sintered magnets were performed in a permeameter after saturation in a pulsed field of 6 T. The microstructures of the magnetic alloys were observed with a scanning electron microscope (SEM) and the phase compositions were determined with the aid of an energy dispersive X-ray (EDX) spectrometer system coupled to the SEM. Corrosion test was carried out according to ASTM B-117 [12].

Table 1 Chemical composition of the starting as-cast alloys.

Alloy nominal composition [at %]	Analyzed composition [wt%]					
	Pr	Fe	Co	B	Nb	Al/Cu
Pr <sub>20.5</sub> Fe <sub>bal</sub> B <sub>5</sub> Cu <sub>2</sub>	40.30	57.57	---	0.57	---	1.56
Pr <sub>16</sub> Fe <sub>76</sub> B <sub>8</sub>	34.20	64.50	---	1.30	---	---
Pr <sub>14</sub> Fe <sub>80</sub> B <sub>6</sub>	30.30	68.62	---	0.99	---	0.09
Pr <sub>14</sub> Fe <sub>79.9</sub> B <sub>6</sub> Nb <sub>0.1</sub>	30.11	68.68	---	0.97	0.14	0.10
Pr <sub>14</sub> Fe <sub>65.9</sub> Co <sub>16</sub> B <sub>4</sub> Nb <sub>0.1</sub>	29.38	55.55	14.23	0.63	0.13	0.08
Pr <sub>14</sub> Fe <sub>64.9</sub> Co <sub>16</sub> B <sub>5</sub> Nb <sub>0.1</sub>	29.95	54.70	14.28	0.83	0.14	0.10
Pr <sub>14</sub> Fe <sub>63.9</sub> Co <sub>16</sub> B <sub>6</sub> Nb <sub>0.1</sub>	30.35	54.11	14.34	0.96	0.14	0.10
Pr <sub>14</sub> Fe <sub>62.9</sub> Co <sub>16</sub> B <sub>7</sub> Nb <sub>0.1</sub>	30.49	53.56	14.48	1.19	0.15	0.13
Pr <sub>14</sub> Fe <sub>61.9</sub> Co <sub>16</sub> B <sub>8</sub> Nb <sub>0.1</sub>	30.49	53.31	14.66	1.30	0.13	0.11
Pr <sub>14</sub> Fe <sub>63.85</sub> Co <sub>16</sub> B <sub>6</sub> Nb <sub>0.15</sub>	30.34	54.01	14.27	1.01	0.23	0.14
Pr <sub>14</sub> Fe <sub>63.50</sub> Co <sub>16</sub> B <sub>6</sub> Nb <sub>0.50</sub>	29.79	54.09	14.40	0.96	0.67	0.09
Pr <sub>14</sub> Fe <sub>64</sub> Co <sub>16</sub> B <sub>6</sub>	30.01	54.56	14.31	1.01	---	0.11

## Results and discussion

The variation in remanence and intrinsic coercivity of HD sintered magnets, produced from a mixture of Pr-based alloys, as a function of boron content, is shown in Figure 1. The best remanence was observed in the Pr<sub>14</sub>Fe<sub>63.9</sub>Co<sub>16</sub>B<sub>6</sub>Nb<sub>0.1</sub> HD sintered magnet (1250±25 mT). The Pr<sub>14</sub>Fe<sub>62.9</sub>Co<sub>16</sub>B<sub>7</sub>Nb<sub>0.1</sub> HD sintered magnet also showed good remanence (1240±25 mT). The highest intrinsic coercivity (987±20 kA/m) was achieved in the sample prepared using the alloy with 8 at% boron. Previous investigation on sintered permanent magnets with similar composition (Pr<sub>15</sub>Fe<sub>62.5</sub>Co<sub>16</sub>B<sub>5.5</sub>Al<sub>1</sub>) reported a remanence of 1270 mT (12.7 kG) and an intrinsic coercivity of 764 kA/m (9.6 kOe) [2, 3].

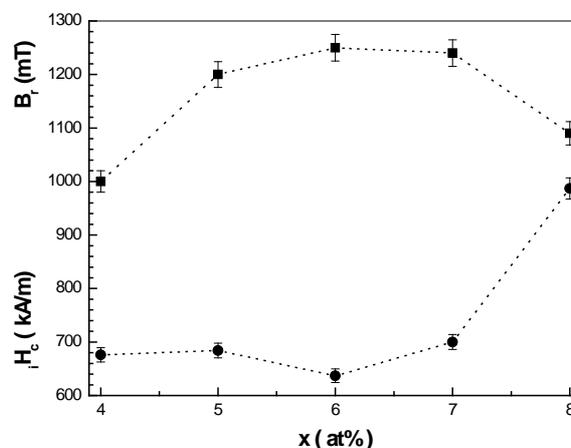


Fig.1- Remanence and intrinsic coercivity versus boron content for Pr<sub>14</sub>Fe<sub>bal</sub>Co<sub>16</sub> B<sub>x</sub>Nb<sub>0.1</sub>-type HD sintered permanent magnets.

A summary of the magnetic properties and the increase in mass due to corrosion of these Pr<sub>14</sub>Fe<sub>bal</sub>Co<sub>16</sub>B<sub>x</sub>Nb<sub>0.1</sub>-type HD magnets is shown in Table 2. The cobalt-free magnet, used for

comparison, exhibited the best intrinsic coercivity but also the highest increase in mass due to corrosion. The highest energy product ( $276 \pm 6 \text{ kJ/m}^3$ ) was observed for the  $\text{Pr}_{14}\text{Fe}_{63.9}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$  magnet together with the best squareness factor ( $\text{SF}=0.75 \pm 0.02$ ). This magnet also exhibited the lowest mass gain due to corrosion indicating a highest corrosion resistance among the tested.

Table 2. Magnetic properties and mass gain due to corrosion of  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_x\text{Nb}_{0.1}$ -type magnets (error:  $\pm 2\%$ ).

Alloy used in the magnet's production	$B_r$ [mT]	$iH_c$ [kA/m]	$bH_c$ [kA/m]	$(BH)_{\text{max}}$ [kJ/m <sup>3</sup> ]	SF [ratio]	Increase in mass [g]
$\text{Pr}_{14}\text{Fe}_{79.9}\text{B}_6\text{Nb}_{0.1}$	1170	1249	836	255	0.68	0.10
$\text{Pr}_{14}\text{Fe}_{65.9}\text{Co}_{16}\text{B}_4\text{Nb}_{0.1}$	1000	676	501	105	0.24	0.05
$\text{Pr}_{14}\text{Fe}_{64.9}\text{Co}_{16}\text{B}_5\text{Nb}_{0.1}$	1200	684	589	249	0.70	0.07
$\text{Pr}_{14}\text{Fe}_{63.9}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	1250	637	549	276	0.75	0.04
$\text{Pr}_{14}\text{Fe}_{62.9}\text{Co}_{16}\text{B}_7\text{Nb}_{0.1}$	1240	700	637	257	0.73	0.06
$\text{Pr}_{14}\text{Fe}_{61.9}\text{Co}_{16}\text{B}_8\text{Nb}_{0.1}$	1090	987	700	210	0.61	0.08

The reduced magnetic properties of the  $\text{Pr}_{14}\text{Fe}_{65.9}\text{Co}_{16}\text{B}_4\text{Nb}_{0.1}$  magnet has been attributed to the presence of a  $\text{Pr}_2\text{Fe}_{17}$  phase in the magnetic alloy even after annealing for homogenization at  $1100^\circ\text{C}$  for 20 h. This 2:17 phase, shown in Figure 2, is the phase slightly darker than the matrix phase. This phase is magnetically soft and detrimental to the magnetic properties of permanent magnets. It is present in lesser amount in the  $\text{Pr}_{14}\text{Fe}_{64.9}\text{Co}_{16}\text{B}_5\text{Nb}_{0.1}$  alloy, as Figure 3 shows. In this case a considerable improvement in remanence, energy product and squareness factor was observed. It disappears in the magnetic alloys with higher boron content. Good overall magnetic properties have been achieved for sintered magnets prepared using 6 and 7 at% B. A comparison between these two micrographs also reveals that in the annealed state the hard magnetic matrix phase ( $\Phi$ ) in the  $\text{Pr}_{14}\text{Fe}_{64.9}\text{Co}_{16}\text{B}_5\text{Nb}_{0.1}$  alloy shows an increased grain size.

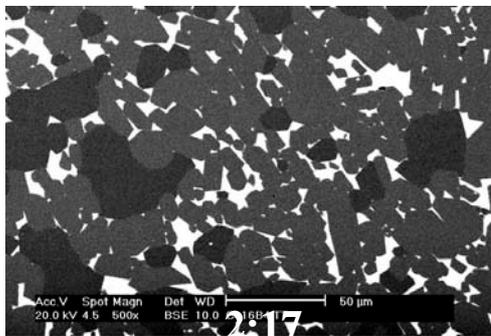


Fig. 2- Backscattered electron image of annealed  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_4\text{Nb}_{0.1}$  alloy.

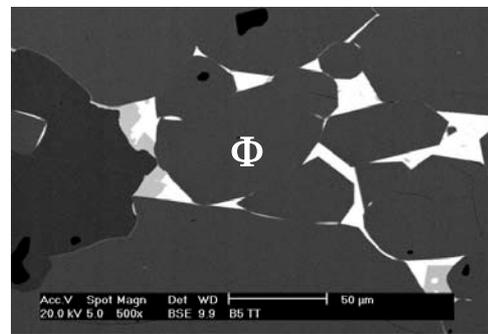


Fig. 3- Backscattered electron image of annealed  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_5\text{Nb}_{0.1}$  alloy.

The microstructure feature of the  $\text{Pr}_{14}\text{Fe}_{64.9}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ , with a more homogeneous structure and less amount of phases, might be responsible for the highest corrosion resistance associated to this magnet. The variation in remanence and intrinsic coercivity of HD sintered magnets, produced from a mixture of Pr-based alloys, as a function of niobium content, is shown in Figure 4. The best remanence was observed for the  $\text{Pr}_{14}\text{Fe}_{63.50}\text{Co}_{16}\text{B}_6\text{Nb}_{0.50}$  HD sintered magnet ( $1340 \pm 27 \text{ mT}$ ) but with a rather low intrinsic coercivity. The highest intrinsic coercivity ( $708 \pm 14 \text{ kA/m}$ ) was achieved in the  $\text{Pr}_{14}\text{Fe}_{64}\text{Co}_{16}\text{B}_6$  HD sintered magnet. A good compromise between these two magnetic properties was found in the magnets containing 0.15 at% Nb.

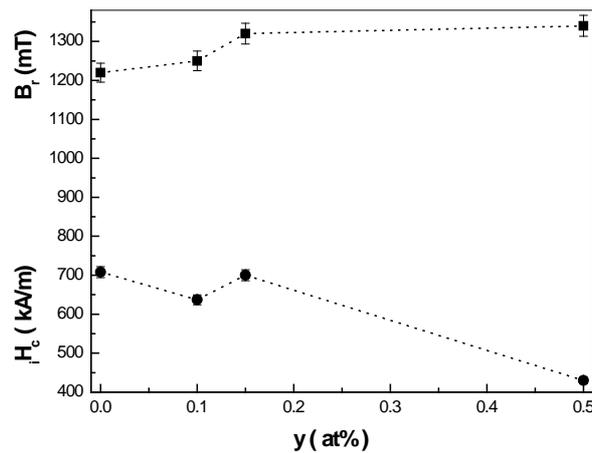


Fig.4- Remanence and coercivity versus Nb content for  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_y$ -type magnets.

A summary of the magnetic properties and the increase in mass due to corrosion of these niobium-containing HD magnets is shown in Table 3.  $\text{Pr}_{14}\text{Fe}_{80}\text{B}_6$  and  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD magnets were included for a comparison. It is worth noting that niobium addition in the magnetic alloy increased the remanence in the HD sintered magnets from  $(1220 \pm 24)$  to  $(1340 \pm 27)$  mT and, in contrast, the intrinsic coercivity decreased considerably in the magnet with 0.50 at% of this element. The highest energy product ( $315 \pm 6 \text{ kJ/m}^3$ ) was exhibited by the  $\text{Pr}_{14}\text{Fe}_{63.85}\text{Co}_{16}\text{B}_6\text{Nb}_{0.15}$  HD magnet, which also showed the best squareness factor ( $\text{SF} = 0.90 \pm 0.02$ ). The lowest corrosion resistance, that is, highest increase in mass due to corrosion was found for the sintered magnets without cobalt and niobium and with the highest rare earth content.

Table 3- Magnetic properties and mass gain due to corrosion of  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_y$ -type magnets (error:  $\pm 2\%$ ).

Alloy used in the magnet's production	$B_r$ [mT]	$iH_c$ [kA/m]	$bH_c$ [kA/m]	$(BH)_{\text{max}}$ [ $\text{kJ/m}^3$ ]	SF [ratio]	Increase in mass [g]
$\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$	1140	1289	867	249	0.87	0.31
$\text{Pr}_{14}\text{Fe}_{80}\text{B}_6$	1230	1050	851	286	0.78	0.13
$\text{Pr}_{14}\text{Fe}_{64}\text{Co}_{16}\text{B}_6$	1220	708	660	272	0.89	0.10
$\text{Pr}_{14}\text{Fe}_{63.9}\text{Co}_{16}\text{B}_6\text{Nb}_{0.10}$	1250	637	549	276	0.75	0.04
$\text{Pr}_{14}\text{Fe}_{63.85}\text{Co}_{16}\text{B}_6\text{Nb}_{0.15}$	1320	700	652	315	0.90	0.08
$\text{Pr}_{14}\text{Fe}_{63.50}\text{Co}_{16}\text{B}_6\text{Nb}_{0.50}$	1340	430	430	146	0.67	0.08

The intrinsic coercivity of the cobalt-containing permanent magnets is reduced when compared to the standard  $\text{Pr}_{14}\text{Fe}_{80}\text{B}_6$  magnet due to the presence of  $\text{Pr}_3(\text{FeCo})$  and  $\text{Pr}(\text{FeCo})_2$  phases in the magnetic alloys. Figure 5 shows backscattered electron images of the annealed  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.15}$  alloy. The white (W) phase is  $\text{Pr}_3(\text{FeCo})$  and the grey (G) is Laves phase  $\text{Pr}(\text{FeCo})_2$ . These cobalt-containing phases remain after the alloy processing to produce the sintered magnet and reduce the intrinsic coercivity. These phases have also been previously identified [13-16].

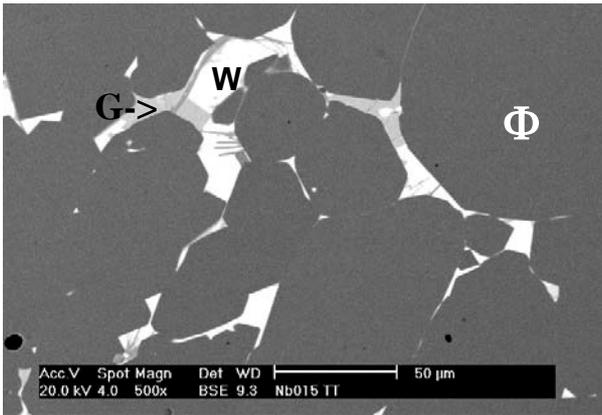


Fig. 5 Backscattered electron image of the annealed  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.15}$  alloy.

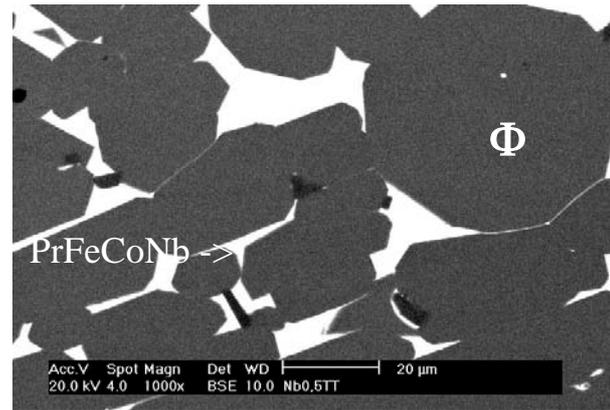


Fig. 6 Backscattered electron image of the annealed  $\text{Pr}_{14}\text{Fe}_{63.50}\text{Co}_{16}\text{B}_6\text{Nb}_{0.50}$  alloy.

The  $\text{Pr}_{14}\text{Fe}_{63.50}\text{Co}_{16}\text{B}_6\text{Nb}_{0.50}$  HD sintered magnet showed a good remanence value ( $1340 \pm 27$  mT) but very low coercivity, energy product and squareness factor. This has been attributed to the small amounts of a Nb-containing phase (54 wt% Nb, 3 wt% Pr, 35 wt% Fe and 8 wt% Co) that were found at the grain boundaries of the cast  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.5}$  alloy, as shown in Figure 6. This phase has also been previously identified [17]. It is important to remind that although the intrinsic coercivity decreases with the addition of cobalt in the alloys, the Curie temperature is considerably enhanced with the addition of this element ( $\sim 11^\circ\text{C}$  per at% Co).

## Conclusions

The results of this study show that the concentration of boron in the Pr-based permanent magnets must be superior to 5 at%. Boron contents lower than 5 at% are detrimental to the magnetic properties of sintered magnets due to the presence of a 2:17 soft ferromagnetic phase with Curie temperature above room temperature. Although the Curie temperature is enhanced, the intrinsic coercivity of the cobalt-containing magnets is reduced due to  $\text{Pr}_3(\text{FeCo})$  and  $\text{Pr}(\text{FeCo})_2$  phases. The addition of 0.15 at% Nb to PrFeCoB-based magnets increases remanence, energy product and squareness factor. A PrFeCoNb phase was detrimental to the magnetic properties of the  $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.5}$  HD sintered magnet. In general, the addition of cobalt and niobium improves the resistance to corrosion of the praseodymium-based HD permanent magnets.

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