THE EFECT OF THE DESORPTION AND RECOMBINATION TEMPERATURE ON THE MAGNETIC PROPERTIES OF HDDR Pr-Fe-Co-B-Nb MAGNETS

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ABSTRACT

This article reports the results of investigations carried out to study the microstructure and magnetic properties of some permanent magnets represented by the formula $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$ *(where x = 0, 4, 8, 10, 12, 16). The magnets were prepared from annealed alloys using the hydrogenation, disproportionation, desorption and recombination (HDDR) process. The effect of the processing temperature (desorption and recombination) upon the magnetic properties and microstructures of these magnets has been investigated. It has been shown that this processing temperature has a significant effect on the magnetic behaviour of these materials.* $Pr_{14}Fe_{80}B_6$ *HDDR magnets have also been prepared for a comparison.*

Keywords: HDDR magnets, Hydrogenation, Pr-Fe-B magnets

INTRODUCTION

The hydrogenation, disproportionation, desorption and recombination (HDDR) process has been successfully employed to produce rare-earth-based bonded magnets. Neodymium based HDDR magnets with high coercivity can be obtained by exposing rare-earth based alloys to hydrogen at elevated temperatures[1-4]. Praseodymium based powders without cobalt has been produced via the HDDR process but with inferior magnetic properties compared to Nd based materials[5]. Lately, it has been show that powders based on the composition

$Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ with good remanence and reasonable coercivity can be produced by this process[6-10]. Cobalt and boron influence were studied in the Pr-Fe-B-Nb HDDR magnets prepared using a similar temperature (860 ºC) for the desorption and recombination[11]. This article reports the results of further work carried out on $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$ alloys (where x = 0, 4, 8, 10, 12, 16). This study was undertaken to optimize the recombination and desorption temperature (800 – 900°C) with respect to the magnetic properties of the HDDR magnets. $Pr_{14}Fe_{80}B_6$ HDDR magnets where prepared for a comparison. The magnetic powders were observed with a scanning electron microscope (SEM).

EXPERIMENTAL PROCEDURE

Commercial alloys in the as-cast state were submitted to a heat treatment in high vacuum (10^{-4} mbar) at 1100°C for 20h. The chemical analyses of the as-cast alloys are given in Table 1. The microstructures of as-cast and heat treated alloys were investigated in a previous work[12]. The as-cast and annealed alloys were crushed into coarse lumps and 9.35 g batches were placed in the HDDR reactor. This reactor was then evacuated to the backing-pump pressure (10^{-1} mbar) and hydrogen introduced until the pressure of 930 mbar.

The temperature of the reactor was held at 100°C for 30 min to provide sufficient time for the hydrogen decrepitation reaction to go to completion. The reactor was then heated to 770°C at 15°C/ min and further up to the desorption temperature 800-900°C at 5°C/ min, with a dwell time of 15 min previously to desorption. The disproportionation occurred approximately at 700°C for all alloys. Subsequent desorption and recombination was carried out under vacuum at the same temperature (800-900°C) until a pressure of 10^{-1} mbar was achieved (7 min). Rapid cooling of the processed 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 106 μm sieve. The fine powder was encapsulated in a small cylindrical rubber bag and pulsed in a magnetic field of 6.0 T and pressed isostatically at 200MPa. The resultant green compacts were consolidated by placing wax in the bag and heating to 80°C to enable the molten wax to penetrate the HDDR powder compact.

The resultant was cooled to room temperature and the excess wax was removed to yield a cylindrical magnet with 1cm^2 area. Measurements in permeameter were performed after saturation in a pulsed field of 6.0 T. The microstructural characterization of the powders and the alloys was carried in a SEM.

Table 1 - The chemical analyses of the as-cast alloys.

Nominal composition (at%)	Composition (wt%)					
	Pr	**Fe**	**Co**	**B**	**Nb**	**Al**
$Pr_{14}Fe_{80}B_6$	30.30	68.62	-	0.99	-	0.09
$Pr_{14}Fe_{80}B_6Nb_{0.1}$	30.11	68.68	-	0.97	0.14	0.10
$Pr_{14}Fe_{bal}B_6Co_4Nb_{0.1}$	30.05	65.16	3.58	0.97	0.15	0.09
$Pr_{14}Fe_{bal}B_6Co_8Nb_{0.1}$	30.29	61.27	7.15	0.96	0.15	0.09
$Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1}$	30.47	59.20	9.03	1.02	0.16	0.12
$Pr_{14}Fe_{bal}B_6Co_{12}Nb_{0.1}$	30.14	57.80	10.83	0.98	0.15	0.10
$Pr_{14}Fe_{bal}B_6Co_{16}Nb_{0.1}$	30.35	54.11	14.34	0.96	0.14	0.10

RESULTS AND DISCUSSION

Figure 1 shows the variation in the remanence of HDDR magnets as a function of the desorption-recombination temperature. Best remanence values were achieved in the $Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1}$ and $Pr_{14}Fe_{bal}B_6Co_{16}Nb_{0.1}$ alloys processed at 800^{o}C and 820^{o}C, respectively. Magnets containing 4 at% Co achieved good values of remanence for the alloy processed at 860°C (Br= 786 mT) and 880°C (Br= 788 mT).

Increasing the cobalt content to 8 at% decreased the magnetic properties although a reasonable value of remanence was obtained for the magnet prepared to 800°C (Br= 737 mT).

In alloy with 10 at% Co a significant increase in remanence was verified. The better results were obtained with composition $Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1.}$ The best result obtained for the $Pr_{14}Fe_{bal}B_6Co_{12}Nb_{0.1}$ alloy was a remanence of 781 mT using a processing temperature of 860°C.

The magnet produced using the $Pr_{14}Fe_{bal}B_6Co_{16}Nb_{0.1}$ and processed at 820°C showed a reasonable remanence (Br= 814 mT).The magnets produced from the $Pr_{14}Fe_{80}B_6$ alloy, used as a comparison showed low remanence.

The alloy $Pr_{14}Fe_{80}B_6Nb_{0.1}$ also exhibited low remanence values. High processing temperature (900 °C) was detrimental for the remanence of the majority

of the HDDR magnets. The best energy product (156.4 kJ/m^3) was achieved with the $Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1}$ magnet, processed at 800°C.

Figure 2 shows the variation in intrinsic coercivity ($_iH_c$) of HDDR magnets as a function of the processing temperature. The HDDR magnet containing 4 at% cobalt, processed at 900°C, exhibited the best intrinsic coercivity (1280 kA/m). This magnetic property decreased independent of the temperature of desorption-recombination for all magnets with higher cobalt content. It is worthwhile noting that the $Pr_{14}Fe_{80}B_6$ HDDR magnet also exhibited a reasonable intrinsic coercivity. The optimum temperatures for obtaining of the good coercivity for the $Pr_{14}Fe_{80}B_6$ and $Pr_{14}Fe_{80}B_6Nb_{0.1}$ alloys were 880°C and 840°C, respectively.

Figure 3 shows the variation in the energy product of HDDR magnets as function of the desorption-recombination temperature. A summary of the magnetic properties of the HDDR magnets produced at distinct temperatures are given in Tables 2-8.

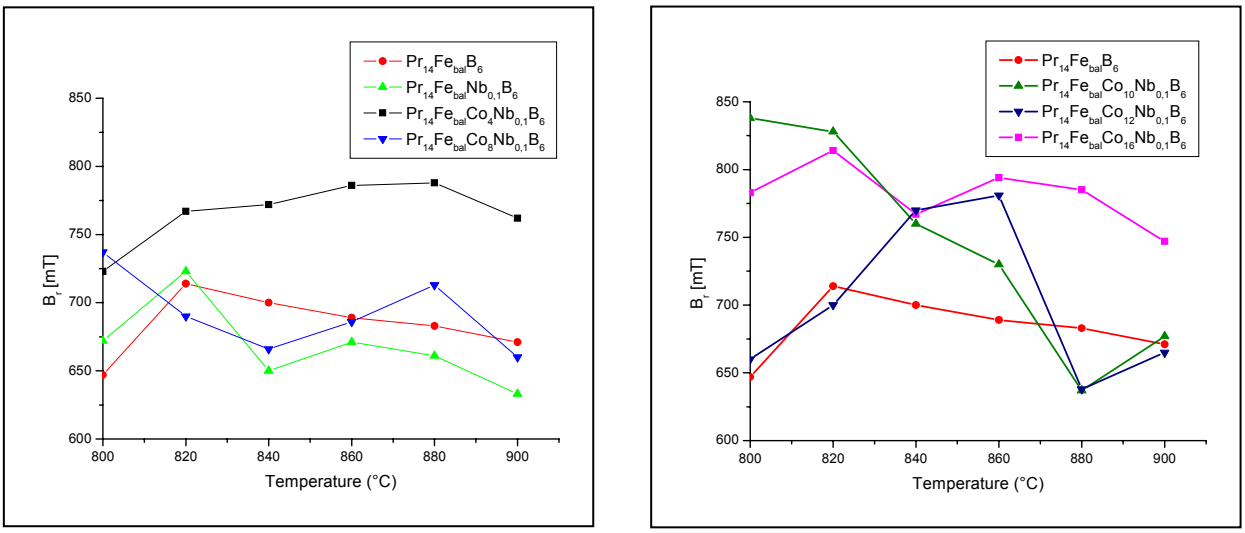


Figure 1 – Remanence versus temperature for the Pr-based alloys.

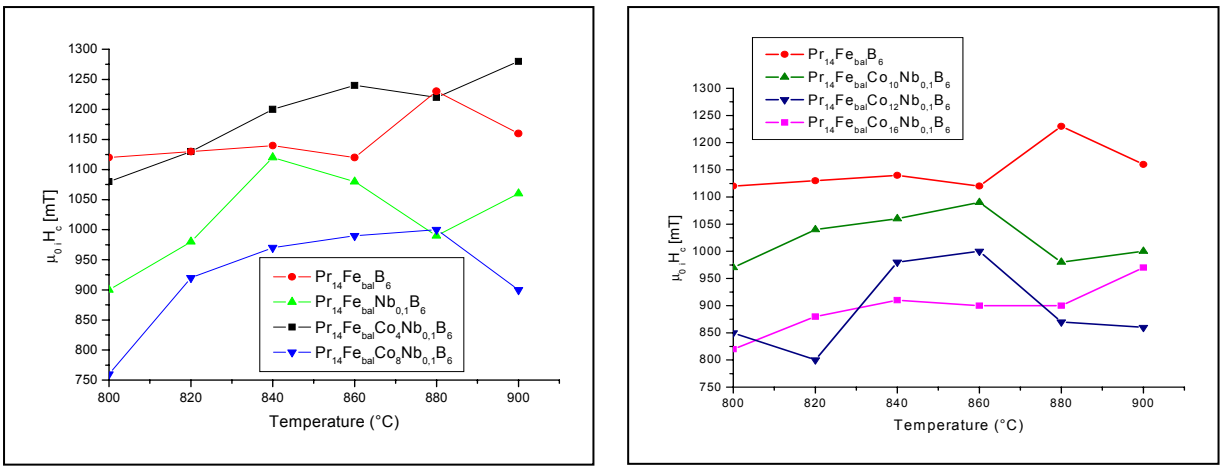


Figure 2 - The intrinsic coercivity of the HDDR magnets as a function of variation in temperature.

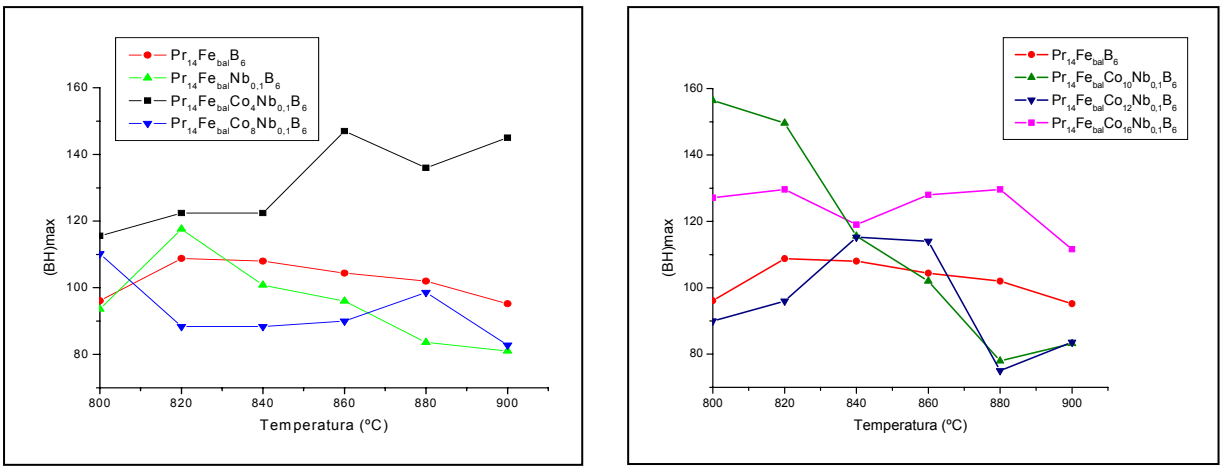
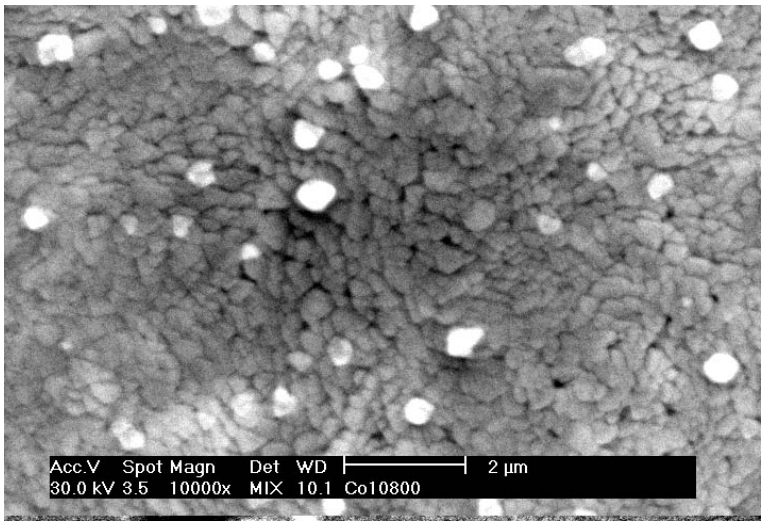
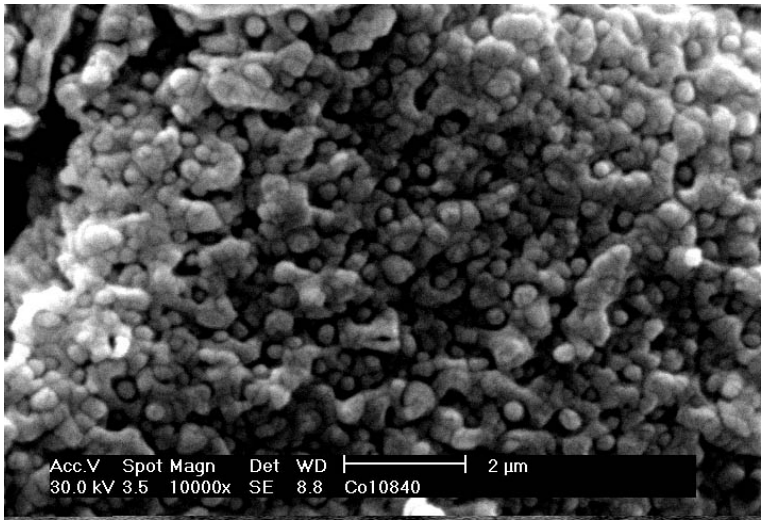


Figure 3 - Variation in the energy product of HDDR magnets as function of the processing temperature.

The microstructures of the $Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1}$ HDDR powders, processed at 800°C and 840°C, are shown in Figure 4 (a) and (b), respectively. It can be clearly seen that for the $Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1}$ alloy the larger the desorption-recombination temperature the larger the grain size.



(a)



(b)

Figure 4 – Backscattered electron image of HDDR material prepared from the homogenized $Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1}$ alloy; (a) 800°C and (b) 840°C. (10000x).

Table 2 – Magnetic properties of $Pr_{14}Fe_{80}B_6$ HDDR magnets processed at 800-900°C (error ± 2%).

$Pr_{14}Fe_{80}B_6$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	647	714	700	689	683	671
$\mu_{0\,i}H_c$ [mT]	1120	1130	1140	1120	1230	1160
$\mu_{0\,b}H_c$ [mT]	540	580	580	550	570	540
(BH)max [kJm^{-3}]	96.1	108.8	108.0	104,4	102.0	95.2
SF [ratio]	0.43	0.35	0.62	0.34	0.34	0.28

Table 3 – Magnetic properties of $Pr_{14}Fe_{80}B_6Nb_{0.1}$ HDDR magnets processed at 800-900°C (error ± 2%).

$Pr_{14}Fe_{80}B_6Nb_{0.1}$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	672	723	650	671	661	633
$\mu_0{}_i H_c$ [mT]	900	980	1120	1080	990	1060
$\mu_0{}_b H_c$ [mT]	500	580	570	540	480	480
(BH)max [kJm^{-3}]	93.6	117.6	100.8	96.0	83.6	81.0
SF [ratio]	0.33	0.42	0.48	0.33	0.24	0.23

Table 4 – Magnetic properties of $Pr_{14}Fe_{75.9}B_6Co_4Nb_{0.1}$ HDDR magnets processed at 800-900°C (error ± 2%).

$Pr_{14}Fe_{75.9}B_6Co_4Nb_{0.1}$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	723	767	772	786	788	762
$\mu_0{}_i H_c$ [mT]	1080	1130	1200	1240	1220	1280
$\mu_0{}_b H_c$ [mT]	570	600	600	620	600	610
(BH)max [kJm^{-3}]	115.6	122.4	122.4	147.0	136.0	145.0
SF [ratio]	0.37	0.57	0.36	0.42	0.35	0.48

Table 5 – Magnetic properties of $Pr_{14}Fe_{75.9}B_6Co_8Nb_{0.1}$ HDDR magnets processed at 800-900°C (error ± 2%).

$Pr_{14}Fe_{bal}B_6Co_8Nb_{0,1}$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	737	690	666	686	713	660
$\mu_0{}_i H_c$ [mT]	760	920	970	990	1000	900
$\mu_0{}_b H_c$ [mT]	500	500	480	500	500	440
(BH)max [kJm^{-3}]	110.2	88.4	88.4	90.0	98.6	82.8
SF [ratio]	0.40	0.28	0.26	0.24	0.24	0.24

Table 6 – Magnetic properties of $Pr_{14}Fe_{75.9}B_6Co_{10}Nb_{0.1}$ HDDR magnets processed at 800-900°C (error ± 2%).

$Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0,1}$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	838	828	760	730	637	677
$\mu_0{}_i H_c$ [mT]	970	1040	1060	1090	980	1000
$\mu_0{}_b H_c$ [mT]	620	640	580	510	440	450
(BH)max [kJm^{-3}]	156.4	149.6	115.6	102.0	78.0	83.2
SF [ratio]	0.45	0.40	0.28	0.22	0.23	0.19

Table 7 – Magnetic properties of $Pr_{14}Fe_{75.9}B_6Co_{12}Nb_{0.1}$ HDDR magnets processed at 800-900°C (error ± 2%).

$Pr_{14}Fe_{bal}B_6Co_{12}Nb_{0.1}$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	660	700	770	781	638	665
$\mu_{0\,i}H_c$ [mT]	850	800	980	1000	870	860
$\mu_{0\,b}H_c$ [mT]	490	490	550	570	420	460
(BH)max [kJm^{-3}]	90.0	96.0	115.2	114.0	75.0	83.6
SF [ratio]	0.36	0.35	0.26	0.33	0.20	0.26

Table 8 – Magnetic properties of $Pr_{14}Fe_{75.9}B_6Co_{16}Nb_{0.1}$ HDDR magnets processed at 800-900°C (error ± 2%).

$Pr_{14}Fe_{bal}B_6Co_{16}Nb_{0.1}$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	783	814	767	794	785	747
$\mu_{0\,i}H_c$ [mT]	820	880	910	900	900	970
$\mu_{0\,b}H_c$ [mT]	500	550	550	550	560	530
(BH)max [kJm^{-3}]	127.1	129.6	119.0	128.0	129.6	111.6
SF [ratio]	0.40	0.42	0.37	0.38	0.42	0.32

CONCLUSIONS

Magnets produced with homogenized $Pr_{14}Fe_{bal}B_6Co_{10}Nb_{0.1}$ alloy yielded the best remanence. The cobalt-free alloys ($Pr_{14}Fe_{bal}B_6$ and $Pr_{14}Fe_{80}B_6Nb_{0.1}$**)** exhibited low values of remanence. Cobalt addition is essential for obtaining good magnetic properties in Pr-based HDDR magnets. Increasing of desorption-recombination temperature there was a substantial grain growth. Magnets with larger grains showed diminished magnetic properties.

ACKNOWLEDGEMENTS

The authors wish to thank FAPESP, CNPQ and IPEN-CNEN/SP for financial support and infrastructure made available to carry out this investigation.

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