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X-Ray Diffraction Analysis and Magnetic Properties of Pr-Fe-B HDDR Powders and Magnets

S. C. Silva[1, a], J. H. Duvaizem[1, b], L. G. Martinez[1, c], M. T. D. Orlando[1, d] R. N. Faria[1, e], H. Takiishi[1, f]

[1]Materials Science and Technology Center -Nuclear and Energy Research Institute, IPEN – CNEN/SP, IPEN-CNEN, 05508900, São Paulo, Brazil
[a]scsilva@ipen.br, [b]jduvaizem@ipen.br, [c]lgallego@ipen.br, [d]mtdorlando@terra.com.br, [e]rfaria@ipen.br, [f]takiishi@ipen.br

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Abstract. Fine magnetic powder has been produced using the hydrogenation disproportionation desorption and recombination (HDDR) process. The first goal of this work involved an investigation of a range of disproportionation/desorption temperatures between 800 and 900°C with the purpose of optimizing the HDDR treatment for a $Pr_{14}Fe_{80}B_6$ alloy. The cast alloy was annealed at 1100°C for 20 hours for homogenization. The optimum disproportionation temperature for achieving high anisotropy was 820°C. The influence of the reaction temperature on the microstructure and magnetic properties of $Pr_{14}Fe_{80}B_6$ HDDR powders and magnets has been shown. A second stage of this study involved the characterization, for each temperature, of the HDDR processed powder using X-ray diffraction analysis. Samples of the HDDR material have been studied by synchrotron radiation powder diffraction using the Rietveld method for cell refinement, phase quantification and crystallite sizes determination. Scanning electron microscopy (SEM) has also been employed to reveal the morphology of the HDDR powder.

Introduction

The hydrogenation disproportionation desorption recombination (HDDR) process is well known as an effective method for producing anisotropic Nd-Fe-B magnetic powders [1]. At present, anisotropic Pr-Fe-B type magnetic powder has been obtained by modifying HDDR process [2-7]. This process is a simple heat treatment, and a specific apparatus other than the furnace which is available for both vacuum and hydrogen atmosphere, are not necessary [8]. The temperature to which the system is submitted to vacuum will have effect on the magnetic properties of the recombinated powder and in the distribution of the particle size [9]. This paper reports the results of the studies that discuss relationships between the structural $Pr_{14}Fe_{80}B_6$ powder characteristics and obtained magnetic properties. The dispropornation/recombination temperature has been optimized (800-900ºC). This investigation was accomplished by X-ray diffraction and scanning electron microscopy analyses.

Experimental procedure

$Pr_{14}Fe_{80}B_6$ commercial alloy in the as-cast state was submitted to a heat treatment in high vacuum (10^{-4} mbar) at 1100°C for 20h. The microstructures of as-cast and heat treated

alloys were investigated in a previous work [10]. The as-cast and annealed alloys were crushed into coarse lumps and 9.35 g batches were placed in a 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 HDDR powder was analyzed in SEM to morphologic studies and X-ray diffraction for analysis of phases and crystallite sizes.
Powder samples were analyzed by synchrotron radiation powder diffraction at the D10B-XPD beamline of the Brazilian Synchrotron Light Laboratory [11]. The measurements were performed in 2θ range from 20° to 110° in 0.01° steps using the wavelength λ = 2.101469 Å. A standard sample of Al_2O_3 [12] was measured in the same conditions for obtaining the instrumental parameters. The XPD data was used for the identification of present phases by means of comparison with [13] and [14] databases.
The powder diffraction data was analyzed by the Rietveld method using the GSAS code [15] under EXPGUI interface [16], using the TCH modified pseudo-Voigh profile function.
The crystallite sizes were determined from the XPD peaks width by the Scherrer method with the correction of instrumental broadening, considering the peak profiles as a convolution of Gaussian and Lorentzian functions (Klug & Alexander).
The phases present in the samples were identified by means of the ICDD-PDF-2 database. Measured diffraction patterns were analyzed by Rietveld refinement in order to quantify the phases and analyze their microstructures using the GSAS package, employing the Thompson-Cox-Hastings profile function. The instrumental parameters were obtained from the refinement of a standard sample of corundum (NIST XRD standard reference materials).

Results and discussions

The magnetic properties of the HDDR magnets processed of $Pr_{14}Fe_{80}B_6$ alloy and produced at distinct temperatures are given in Table 1. The optimum reaction (desorption/recombination) temperature for obtaining of the good remanence for the $Pr_{14}Fe_{80}B_6$ alloy was 820°C (714mT). The HDDR magnet processed of $Pr_{14}Fe_{80}B_6$ alloy, processed at 880°C, exhibited the best intrinsic coercivity (1230 kA/m). The results of the Rietveld refinements of the HDDR powders produced using the $Pr_{14}Fe_{80}B_6$ alloy is given in Table 2.

Table 1 – Magnetic properties of $Pr_{14}Fe_{80}B_6$ HDDR magnets processed at 800-900°C.

$Pr_{14}Fe_{80}B_6$	Temperature [^{0}C]					
	800	**820**	**840**	**860**	**880**	**900**
B_r [mT]	625	714	700	689	683	671
$\mu_{0\,i}H_c$ [mT]	1060	1130	1140	1120	1230	1160
$\mu_{0\,b}H_c$ [mT]	510	580	580	550	570	540
(BH)max [kJm^{-3}]	84,1	108,8	108,0	104,4	102,0	95,2
FQ [razão]	0,35	0,35	0,35	0,34	0,34	0,28

Table 2 – Results of the Rietveld refinements of XRD data.

Temperature	**Chi^2**	**RF^2**	**[%] PrFeB**	**a (Å)**	**c (Å)**	**Other phases**
Pr800	1.810	2.78	91.7	8.813669	12.256165	Pr_2O_3 7.0 % PrH 1.2 %
Pr820	1.929	5.77	98.2	8.804298	12.249772	Pr_2O_3 1.8 %
Pr840	1.661	4.59	95.4	8.803664	12.248670	Pr_2O_3 4.6 %
Pr860	1.755	4.56	98.8	8.804291	12.248882	Pr_2O_3 1.2 %
Pr880	1.892	4.06	98.6	8.803509	12.248175	Pr_2O_3 1.4 %
Pr900	1.763	5.67	98.6	8.803494	12.248116	Pr_2O_3 1.4 %

Figure 1 shows the variation in the remanence of HDDR magnets as a function of the desorption-recombination temperature. HDDR magnets processed at 800°C presented low remanence value. Increasing the reaction temperature can be observed the decrease in the remanence values. The calculated values of mean crystallite sizes are shown in Table 3. With an increase in the reaction temperature the values of mean crystallite size were also increased. Low values of remanence were observed for desorption/ recombination temperatures of 800°C and 900°C. This shows that small or large crystallite sizes are detrimental to the magnetic properties. It is very likely that each alloy has an ideal crystallite size for achieve good remanence and coercivity, accordingly to the reaction temperature. In this case the best remanence was exhibited for a desorption/ recombination temperature of 820°C. Therefore, the ideal crystallite size that led to these magnetic properties is 156nm.

The XRD results reveal the presence of a small amount of praseodymium oxide Pr_2O_3 for all samples. This oxide is probably formed by the reaction of the material with atmospheric oxygen after the synthesis. For the sample treated at 800° C, it was found also a small amount of praseodymium hydride PrH, indicating that this temperature was ineffective for complete dehydrogenation.

Table 3 – Values of mean crystallite size.

Sample Temperature [°C]	Mean crystallite size [nm]
800	62
820	156
840	172
860	209
880	226
900	264

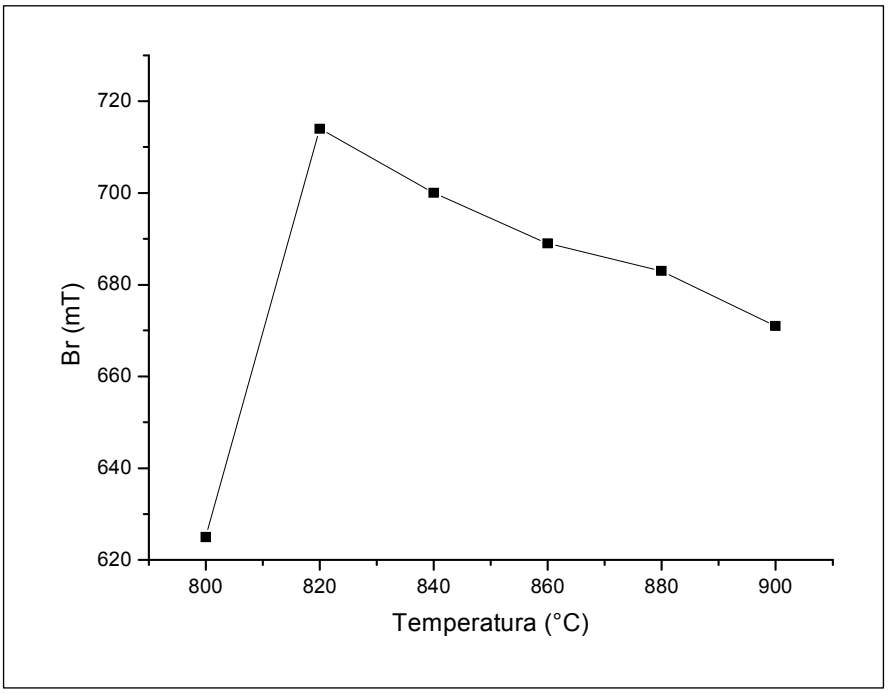

Fig. 1 - Variation in the remanence of HDDR magnets as a function of the reaction temperature.

The microstructures of the HDDR powder obtained from the homogenized Pr-based alloys are shows in Figures 2 (a-f). It can be observed that, with the increase of the reaction temperature from 800°C up to 900°C, there was also a stead increase in the grain size and, hence, a decrease in the intrinsic coercivity. This is consistent with the previous XRD results.

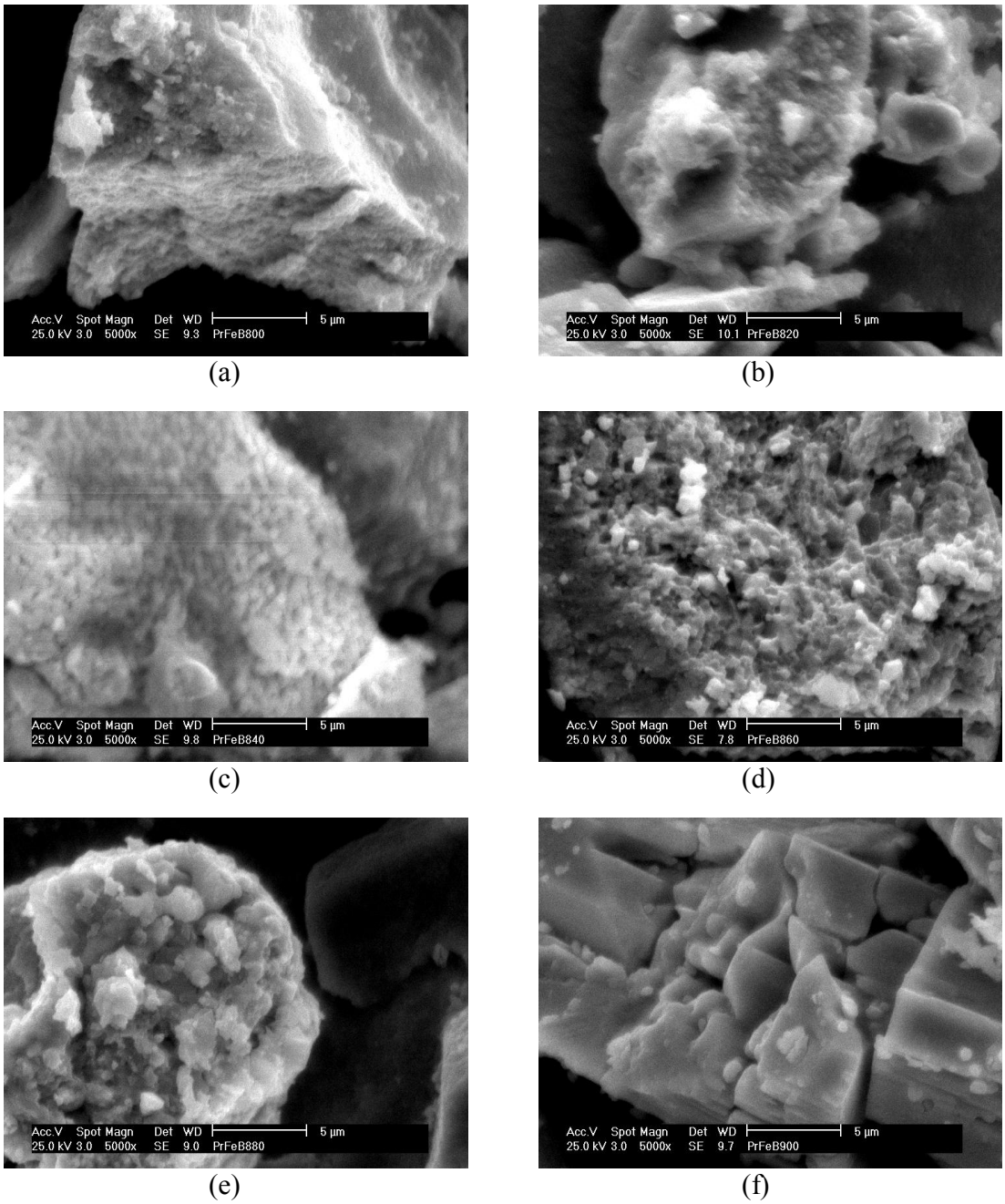

Fig. 2 – Microstructures of the $Pr_{14}Fe_{bal}B_6$ HDDR powders: (a) 800°C; (b) 820°C; (c) 840°C; (d) 860°C; (e) 880°C and (f) 900°C. (5000x).

Conclusions

The best remanence was achieved for the HDDR magnet prepared from the annealed $Pr_{14}Fe_{80}B_6$ alloy processed at 820°C and best coercivity was obtained at 880°C. The crystallite size for optimum remanence was 156nm. This shows that each alloy possesses an ideal crystallite size which is related with the desorption/ recombination temperature. The lower reaction temperature (800°C) is ineffective to powder processing since it was found a small amount of praseodymium hydride in this material, indicating insufficient dehydrogenation.

The microstructures of the HDDR powders revealed an increase in grain size when the reaction temperature increased from 800°C to 900°C.

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