

## The Influence of Praseodymium Content on the Hydrogen Absorption Capability of PrFeCoBNb magnetic alloys

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**Keywords:** Hydrogen absorption, Pr-alloys, PrFeB, magnets.

**Abstract.** The hydrogen absorption capability of  $\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  ( $12.0 \leq x \leq 14.0$ ) magnetic alloys was evaluated. A practical methodology was developed so that the hydrogen pressure decrease inside a closed system was correlated to the mass gain (% $W$ ) of the sample. % $W$  increases linearly with the Pr concentration in the magnetic alloy either in the as-cast state or annealed during 20 hours at 1070°C. Comparisons between % $W_{theoretical}$  and % $W_{experimental}$  showed a satisfactory agreement.

### Introduction

The hydrogen decrepitation (HD) process can be used during the production of REFeB (RE = Nd or Pr) sintered magnets [1]. It occurs in two distinct stages. Firstly, hydrogen is absorbed by the RE-rich phase located at the grain boundaries and then by the hard magnetic phase [2-3]. The magnetic properties of sintered magnets are usually changed by modifying the alloy chemical composition. However, such modification also influences the total amount of hydrogen absorbed by the raw material. This occurs due to the alteration of the RE-rich phase amount or even to the presence of new phases. DTA (differential thermal analysis) measurements show that the  $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$  alloy readily absorbs hydrogen at room temperature with an exothermic reaction [4]. In this work the hydrogen absorption of PrFeCoBNb alloys with several rare earth contents was studied.

### Experimental

$\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  ( $12.0 \leq x \leq 14.0$  – nominal composition) alloys in the as-cast state or annealed at 1070 °C for 20 hours were used in this investigation. To perform the HD process, (20.00 ± 0.01)g of the bulk ingot were placed in a stainless steel vessel which was evacuated to backing-pump pressure to cleaning. Hydrogen was then introduced in the system at 298K to a pressure of  $2 \times 10^5$  Pa (2 bars).

To evaluate the mass gain by each alloy it was used the ideal and the real gases equations. For the former:

$$n_i = \frac{RT_i}{P_i V_i} \quad (1)$$

where  $n_i$ ,  $P_i$  and  $T_i$  are number of mols, the  $\text{H}_2$  pressure and temperature before the beginning of the absorption process, respectively,  $V$  is the volume of system which encloses the gas and  $R$  is the universal constant of gases. It is worth pointing out that the volume of the system does not change during the HD process. Therefore, in this case, the hydrogenation can be considered independent on

$V$ . On the other hand, it is well known that the hydrogen absorption by REFeB alloys causes a temperature increase of the sample. In order to obtain the calculations independent on  $T$ , it is necessary that  $T_i$  e  $T_f$  are the same [5]. Such condition is satisfied using the room temperature (RT) because this is the temperature before and after the HD process. However, for the latter,  $T_f = RT$  after a period of time much longer compared to the duration of the HD process. Based on these considerations, it is possible to write:

$$n_f = n_i \left( \frac{P_f}{P_i} \right) \quad (2)$$

where  $n_f$  and  $P_f$  are the final number of mols and the  $H_2$  pressure in the system, respectively. Regarding the real gases equation, the number of mols of hydrogen in the system was determined using the well known Van der Waals equation [6, 7]:

$$\left( P_i + \frac{n_i^2 a}{V_i^2} \right) (V_i - n_i b) = n_i R T_i \quad (3)$$

where  $a$  and  $b$  are constants referent to  $H_2$ . After the absorption process, one may write:

$$n_f = n_i \frac{P_f V_f}{(P_i V_i - P_i n_i b + n_i P_f b)} \quad (4)$$

The same assumptions considered for the ideal gases equation were applied in this situation. For both cases, the quantity of absorbed hydrogen by the sample, in mols, will be given by:

$$W_{H_2} = n_i - n_f \quad (5)$$

The absorbed hydrogen mass is found multiplying  $W_{H_2}$  and the molecular mass of  $H_2$ , identified from now on as  $W$ . A general way to present this result is normalize  $W$  by the sample mass ( $m$ ) of the alloy:

$$\%W = \frac{W}{m} \times 100. \quad (6)$$

X-ray diffraction (XRD) measurements were carried out using Cu-K $\alpha$  radiation from 20° to 50° at a scanning rate of 0.5°/min. Magnetic measurements were obtained using a vibrating sample magnetometer (VSM) using a maximum field of 20 kOe (2.0 T) at room temperature.

## Results and discussion

The  $\%W$  values as a function of the Pr-content in the samples are shown in Fig. 1. The increase in the rare earth amount is followed by a linear increase of the hydrogen absorption both in the as-cast and the annealed alloys. However,  $\%W$  for the annealed alloys was somewhat smaller than that observed for the as-cast samples. This is attributed to the lower RE-rich phase amount in the alloy after annealing [8] due to the peritectic reaction between Fe- $\alpha$  and RE-rich phase, which the  $RE_2(Fe, Co)_{14}B$  phase is obtained.

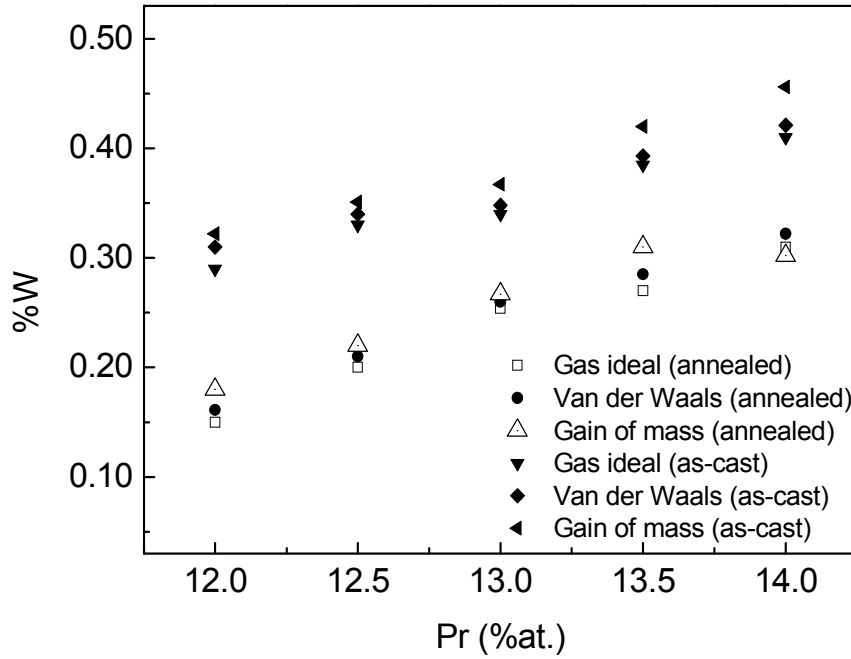


Fig. 1 – %W as a function of Pr-content of  $\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  ( $12 \leq x \leq 14$ ) alloys.

The structure of  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  powders, prepared from alloys before and after annealing, is shown in Fig. 2 and 3 respectively. Particles in the annealed samples are somewhat bigger compared to the cast state samples. This is attributed to the grain growth on annealing. Besides, it is verified that the particles show flat surfaces in both cases, an indicative the fracture occurs by cleavage.

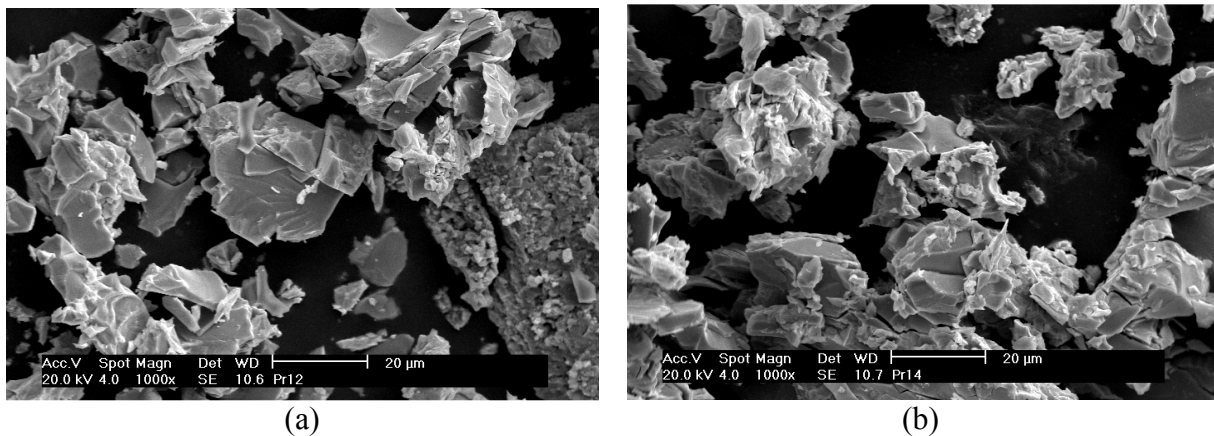


Fig. 2 – SEM images of the hydrogenated cast alloys: a)  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and b)  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$

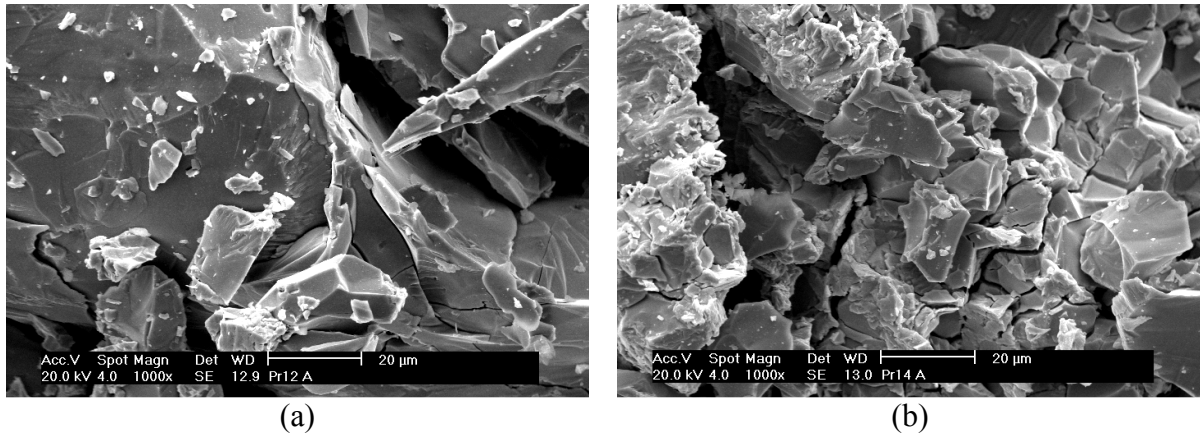


Fig. 3 – SEM images of hydrogenated annealed alloys: a)  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and b)  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$ .

X-ray diffraction patterns for the  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  alloys in the as-cast state and after annealing are shown in Fig. 4 and 5, respectively. The  $2\theta$  angle variation found for these alloys ( $\leq 0.1^\circ$ ), compared to the same phase with no H in the structure, are consistent with a previous study [9]. Free iron was undetected in the annealed alloys. The hysteresis curves for the hydrogenated samples in the cast state and after annealing are shown in Fig. 6 and 7, respectively. Loops with reduced intrinsic coercivity were obtained due the reduction of the magnetocrystalline anisotropy of the hard magnetic phase in the hydrogenated state

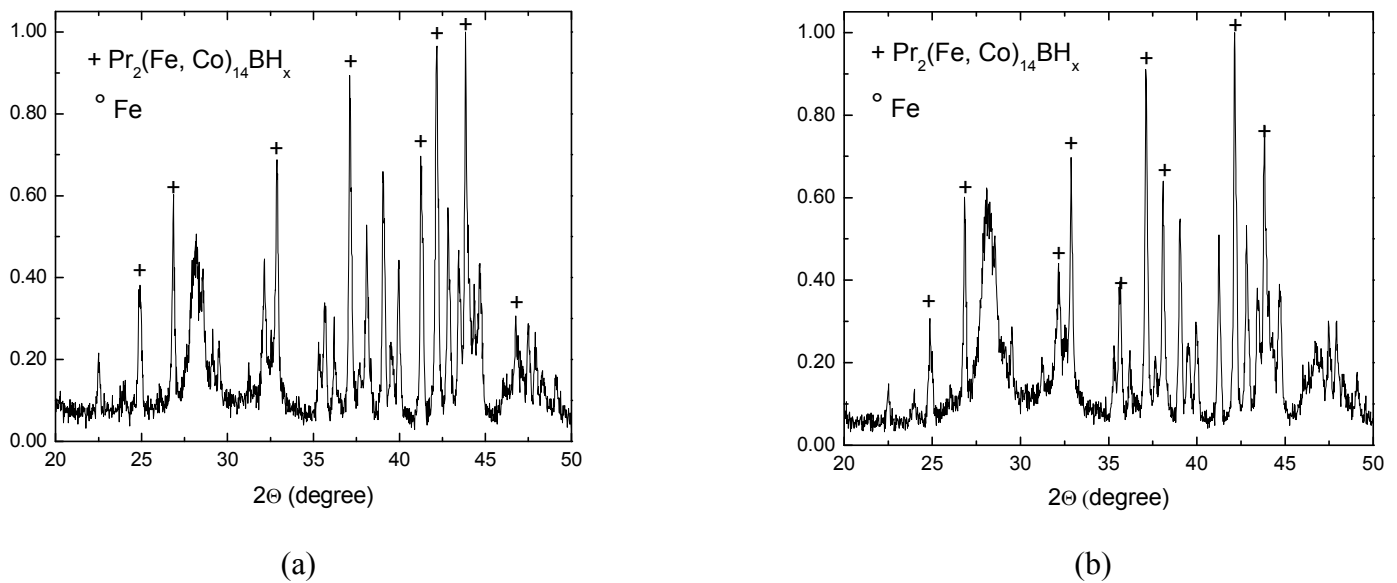


Fig. 4 – XRD patterns for the hydrogenated cast alloys: a)  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and b)  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$

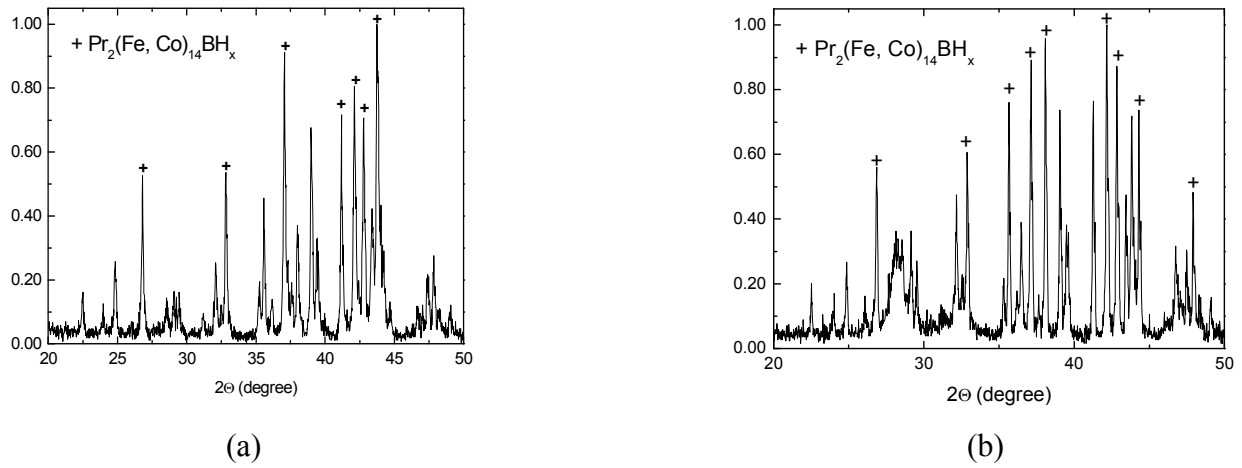


Fig. 5 – XRD patterns for the hydrogenated annealed alloys: a)  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and b)  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$

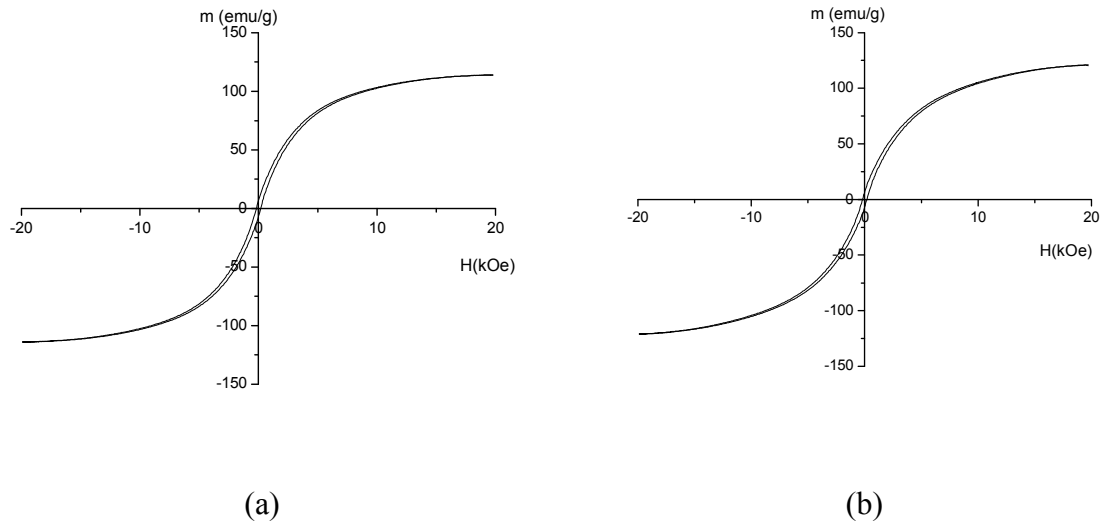


Fig. 6 – Hysteresis loops for the hydrogenated cast alloys: a)  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and b)  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$ .

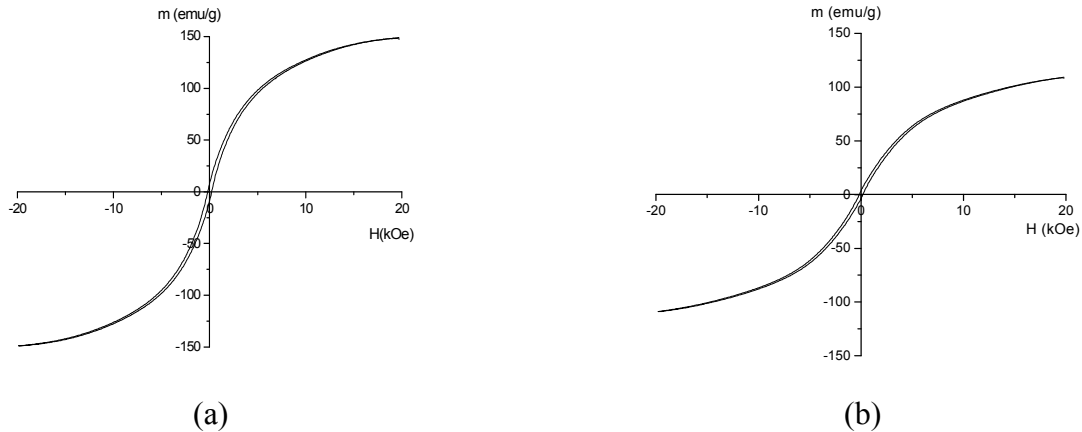


Fig. 7 – Hysteresis loops for the hydrogenated annealed alloys: a)  $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  and b)  $\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$ .

## Conclusions

The mass gain in  $\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16.0}\text{B}_{6.0}\text{Nb}_{0.1}$  ( $12 \leq x \leq 14$ ) alloys can be calculated by using the law of ideal gases utilizing hydrogen pressures of  $2 \times 10^5$  Pa at room temperature. The hydrogen absorption in these alloys increases linearly with the amount of praseodymium. After annealing the quantity of absorbed hydrogen diminished considerably and this was attributed to the smaller amount of Pr on the annealed alloy.

## Acknowledgements

The authors thank the National Council for Scientific and Technological Development (CNPq), The State of São Paulo Resource Foundation (FAPESP – contract 05/04711-2) and the Energy and Nuclear Research Institute (IPEN) for the financial support and infrastructure which made available this investigation. The authors are also indebted to S. Romero for the VSM analyses.

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## **Advanced Powder Technology VII**

doi:10.4028/www.scientific.net/MSF.660-661

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doi:10.4028/www.scientific.net/MSF.660-661.296