Microstructure and Magnetic Properties of PrFeCoBNb Sintered Magnets Produced From HD and HDDR Powders

E. A. Ferreira [a], S. C. Silva [b], E. A. Périgo [c], R. N. Faria [d], H. Takiishi [e]

Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brazil

[a] email: eaferreira@ipen.br, [b] email: scsilva@ipen.br, [c] email: eaperigo@ieee.org,

[d] email:rfaria@ipen.br, [e] email: takiishi@ipen.br

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Abstract. Sintered magnets have been produced with powder obtained using the hydrogenation, disproportionation, desorption and recombination process (HDDR). The new processing procedure for the production of the sintered magnets has been adopted in an attempt to reduce the milling time. Commercial cast ingot alloys based on the compositions $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ and $Pr_{20.5}Fe_{bal}B_5Cu_{2.0}$ have been employed in this investigation. The HDDR powder was used to produce sintered magnets using a mixture of these alloys, in very distinct proportions. Only a small amount (20 wt. %) of the copper-containing alloy has been added as a sintering aid. Standard hydrogen decrepitation (HD) magnets have also been included in this work for a comparison. The effect of a reduced milling time on the magnetic properties of the HDDR sintered magnets has been investigated. Sintering temperature and time of were kept constant for all magnets (1050ºC for 60 minutes). The microstructures of the permanent magnets have been investigated by scanning electron microscopy and energy dispersive X-ray analysis.

Introduction

Currently, PrFeB-based sintered magnets with good magnetic properties have been produced using the hydrogen decrepitation process. The hydrogenation, disproportionation, desorption and recombination process, developed for Nakayama and Takeshita [1] in 1989, is a traditional method that become attractive in the production of magnetically coercive powders. Furthermore, HDDR magnets based on praseodymium-iron-cobalt revealed to be much easier to prepare [2]. The influence of the milling time on the magnetic properties of sintered magnets has been studied in several works [3,4,5]. In this study, sintered HD magnets have been produced using a mixture of two alloys: $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ (80 wt.%) and $Pr_{20.5}Fe_{bal}B_5Cu_{2.0}$ (20 wt.%) .These magnets have been prepared using conventional powder metallurgy and the HD process, with a milling time fixed in 20 hours. Using the same mixture, the HDDR process was employed in three distinct processing routes, aiming the reduction of the milling time used in the standard HD procedure.

Experimental Procedure

The production of HD sintered magnets used two cast alloys with the following composition: $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ and $Pr_{20.5}Fe_{bal}B_5Cu_{2.0}$, milled for 20 hours. Prior processing the magnets, the alloy $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ was homogenized at 1070°C for 20 hours. No heat treatment was applied to the $Pr_{20.5}Fe_{bal}B_5Cu_{2.0}$ alloy, employed as sintering aid. This standard procedure, using the sequence shown in Fig.1, was used as reference for the study of the other three processing routes with the HDDR process (route A, B and C). The sintering step, for all magnets, was carried out at 1050°C for 1 hour.

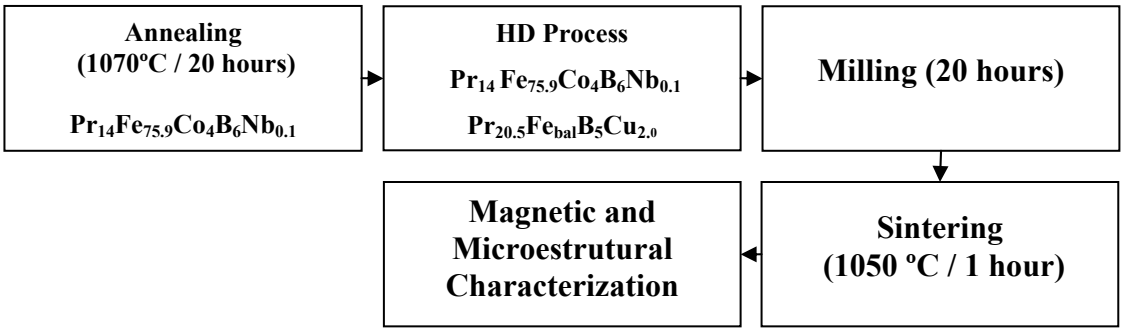


Figure 1 - Standard HD sintered magnets processing route.

The second route (A) used the processes HDDR and HD for obtaining of the magnetic powders. The same mixture of starting alloys was also used in this case (80/20 wt%). The process HDDR was carried out, however, only in the $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ alloy. Subsequently, the process HD was conducted with a mixture of these materials, as shown in Fig. 2.

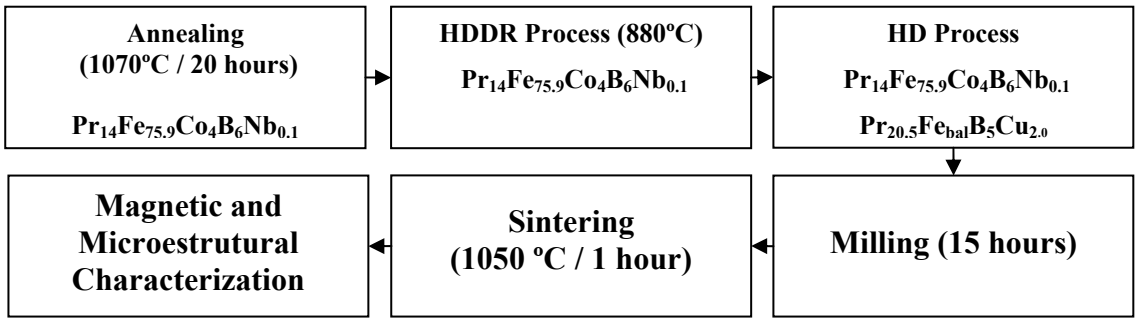


Figure 2 – Sequence for the production of magnets using route A.

In the third route (B) sintered magnets were produced using only the HDDR process to yield the magnetic powders and employed a milling time of 10 hours. The process HDDR was carried out, however, directly in the mixture of the starting alloys. The processing sequence is illustrated in Fig. 3.

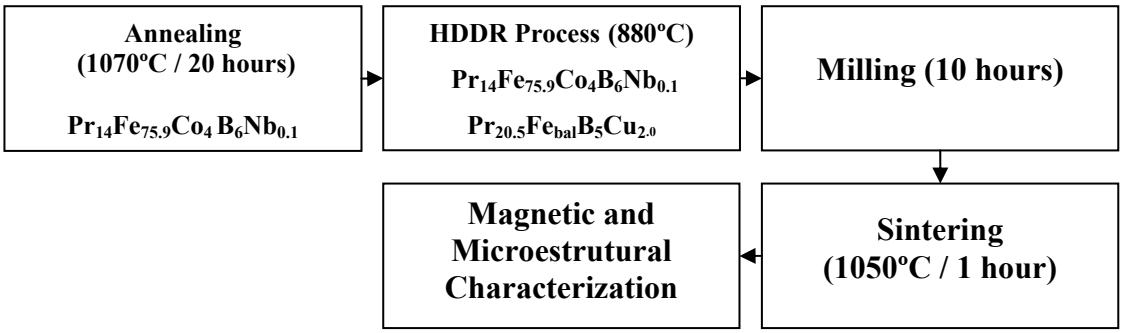


Figure 3 – Sequence for the production of magnets using route B.

In the last route investigated in this study (C), the sintered magnets were prepared using the HDDR and HD processes subsequently, as illustrated in Fig. 4. In this case a very short milling time was employed (5 hours).

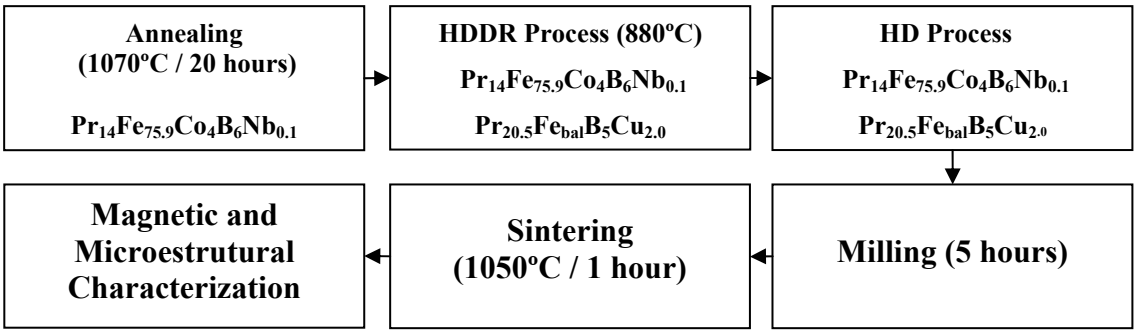
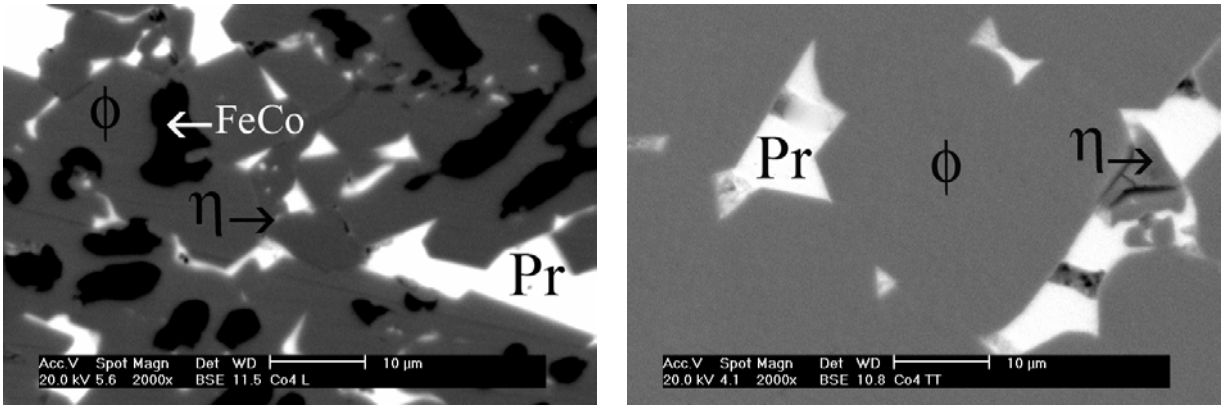


Figure 4 – Sequence for the production of magnets using route C

Results and Discussion

The microstructures of the $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ alloy before and after the annealing are shown in Fig. 5 (a) and (b), respectively. The $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ alloy is composed of the matrix phase $Pr_2(FeCo)_{14}B$ (ϕ), praseodymium-rich phase $Pr_3(FeCo)$, boron-rich phase ($Pr_{1+\varepsilon}Fe_4B_4$ or η) and FeCo (free-iron /cobalt or α-FeCo). The $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ alloy after the annealing is composed of the matrix phase $Pr_2(FeCo)_{14}B$ (ϕ), praseodymium-rich phase $Pr_3(FeCo)$ and boron-rich phase ($Pr_{1+\varepsilon}Fe_4B_4$ or η).



(a) (b)

Figure 5 - Microstructures of the $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ alloy (a) before the annealing and (b) after the annealing, (2000x).

The chemical compositions of the phases determined by EDX on a SEM for the $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ alloy before and after the annealing are given in Table 1. The boron rich phase $Pr_{1+\varepsilon}Fe_4B_4$ (η) was identified by Fe:Pr ratio [6]. The free-iron/cobalt phase (FeCo), present in the alloy, is not present after the annealing treatment at 1070ºC for 20 hours. On annealing, the iron and the cobalt atoms (smaller than Pr) diffused through the matrix phase and reacted with the atoms of Pr and B, forming the phase (ϕ) [7]. The magnetic properties and densities of all $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ sintered permanent magnets are given in Table 2.

Table 1 – Composition determined by EDX of the phases present in the $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ alloy, before and after the annealing.

Alloy $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$	Phase	Chemical composition (at. %) Pr	Fe	Co
before annealing	$Pr_2(FeCo)_{14}B$ (ϕ)	14.5 ± 0.1	80.8 ± 0.2	4.7 ± 0.1
	$Pr_3(FeCo)$ (Pr rich)	81.0 ± 0.2	17.7 ± 0.2	1.3 ± 0.4
	$Pr_{1+\varepsilon}Fe_4B_4$ (η)	22.4 ± 0.2	77.6 ± 0.4	-
	FeCo	3.1 ± 0.1	87.1 ± 0.3	8.6 ± 0.3
after annealing	$Pr_2(FeCo)_{14}B$ (ϕ)	13.4 ± 0.3	79.7 ± 0.2	4.9 ± 0.3
	$Pr_3(FeCo)$ (Pr rich)	79.9 ± 0.1	14.2 ± 0.2	4.6 ± 0.2
	$Pr_{1+\varepsilon}Fe_4B_4$ (η)	22.1 ± 0.5	77.5 ± 0.1	-

Table 2 – Magnetic properties of the $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ HD/HDDR sintered magnets produced using the various processes.

Route	Milling Time (h)	B_r (T) (± 0.02)	$\mu_0{}_iH_c$ (T) (± 0.02)	$\mu_0{}_bH_c$ (T) (± 0.02)	$(BH)_{max}$ (kJ/m^3) (± 2)	SF (± 0.02)	ρ (g/cm^3) (± 0.02)
Standard	20	1.22	1.19	0.89	283	0.88	7.38
A	15	0.88	0.60	0.33	82	0.33	6.93
B	10	0.94	0.64	0.39	89	0.45	7.09
C	5	1.14	1.02	0.81	241	0.83	7.31

The microstructures of the HD/HDDR sintered magnets prepared employing various process and milling times are shown in Figs. 6 (a-d), standard HD and routes A, B and C, respectively. The phases found in the sintered magnets are identified in the micrographics. Four phase were identified: the matrix phase (ϕ), the Pr rich in the grain boundaries of the matrix phase, the boron rich phase $Pr_{1+\varepsilon}Fe_4B_4$ (η) and the Laves Phase $Pr(FeCo)_2$. The Laves phase was only found in magnets processed using routes A and B. Despite the somewhat lower density of the magnets prepared with these two routes, porosity was not clearly visible in their microstructures.

It has been reported that the Laves phase $Pr(FeCo)_2$ is detrimental to the intrinsic coercivity of Rare-Earth-based sintered magnets [8]. In the present study it was deleterious to all magnetic properties. This phase is localized in the grain boundary of matrix phase together with the Pr-rich phase and was not identified in the magnets prepared using the standard process and route C (see Fig. 6 a and d). The chemical compositions of the phases determined by EDX for $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ magnets are given in Table 3.

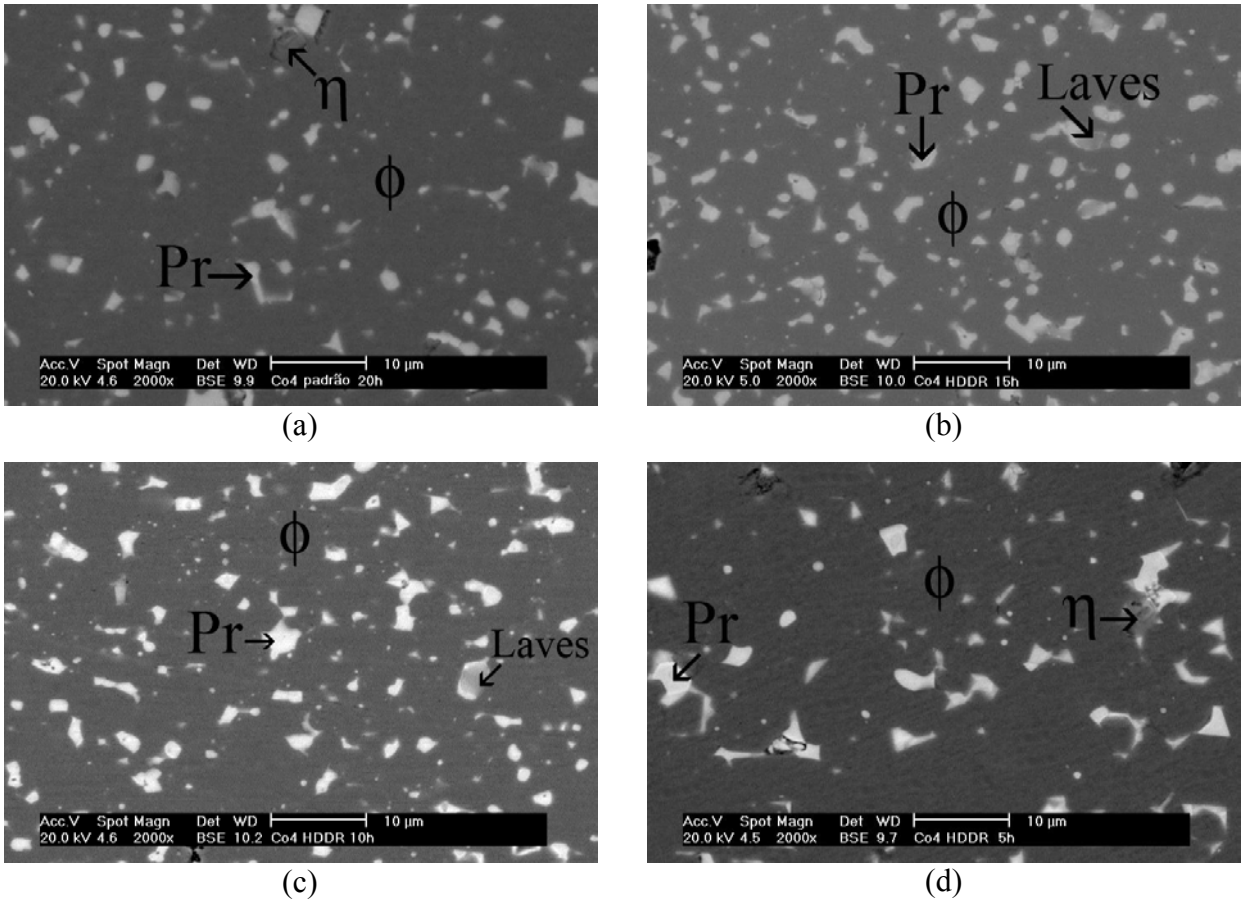


Figure 6 - Microstructures of the Pr-based sintered magnets: (a) standard HD process and (b-d) routes A-C, respectively; (2000x).

Table 3 - Chemical composition determined by EDX for the phases present on the $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ magnets.

Route	Milling time (h)	Phase	Chemical composition (at. %)		
			Pr	Fe	Co
Route Standard (HD)	20 hours	$Pr_2Fe_{14}B$ (ϕ)	13.8 ± 0.1	82.3 ± 0.3	4.0 ± 0.1
		Pr_3(FeCo) (Pr rich)	80.6 ± 0.4	17.6 ± 0.2	1.8 ± 0.2
		$Pr_{1+\varepsilon}Fe_4B_4$ (η)	22.4 ± 0.4	77.6 ± 0.3	-
Route A (HDDR/HD)	15 hours	$Pr_2Fe_{14}B$ (ϕ)	13.7 ± 0.2	81.8 ± 0.3	4.5 ± 0.2
		Pr_3(FeCo) (Pr rich)	80.7 ± 0.1	17.6 ± 0.4	1.7 ± 0.2
		$Pr(FeCo)_2$ (Laves)	55.1 ± 0.1	42.9 ± 0.1	2.0 ± 0.2
Route B (HDDR)	10 hours	$Pr_2Fe_{14}B$ (ϕ)	13.8 ± 0.1	81.7 ± 0.2	4.5 ± 0.3
		Pr_3(FeCo) (Pr rich)	80.5 ± 0.2	17.6 ± 0.5	1.9 ± 0.1
		$Pr(FeCo)_2$ (Laves)	54.8 ± 0.2	43.1 ± 0.1	2.3 ± 0.2
Route C (HDDR/HD)	5 hours	$Pr_2Fe_{14}B$ (ϕ)	13.6 ± 0.2	81.7 ± 0.1	4.7 ± 0.1
		Pr_3(FeCo) (Pr rich)	80.5 ± 0.3	17.4 ± 0.3	2.1 ± 0.1
		$Pr_{1+\varepsilon}Fe_4B_4$ (η)	21.9 ± 0.1	78.1 ± 0.3	-

Conclusions

For a particular processing route, the HDDR process can be included in the production of sintered Pr-based HD magnets to reduce considerably the milling time. In this route (C), the mixture of the main alloy ($Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$) and a sintering aid alloy ($Pr_{20.5}Fe_{bal}B_5Cu_{2.}$) have been processed together in the HDDR and HD steps. A slightly diminution in the magnetic properties (B_r = 1.14 T and $\mu_{0i}H_c$ = 1.02 T) have been observed in these magnets compared to those produced using the standard HD processing route (B_r = 1.22 T and $\mu_{0i}H_c$ =1.19 T). The presence of the phase of Laves and the low density exhibited in the magnets of the route A and B were detrimental to the magnetic properties.

Acknowledgments

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