The Effect of Milling Time upon Microstructures of Pr-Fe-B HD Sintered Magnets Prepared by a Low-Cost Powder Technique

E. P. Soares[1], E. A. Ferreira[1], E. A. Périgo[1], H. Takiishi[1], R. N. Faria[1]

Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP.

Av. Prof. Lineu Prestes, 2242 - CEP 05508-000, Brazil

epsoares@ipen.br, eaferreira@ipen.br, eaperigo@ieee.org, takiishi@ipen.br, rfaria@ipen.br

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Abstract: $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$ magnets have been produced using a combination of the hydrogen decrepitation (HD) process and a powder transfer technique. Sintered magnets have been prepared using HD powders ball milled from 9 to 36 hours. The effects of the milling stage upon microstructure have been investigated. In the $Pr_{17}Fe_{79}B_4$ magnets four phases have been identified: $Pr_2Fe_{14}B$ (Φ), Pr rich, Pr_2Fe_{17} and Laves phase ($PrFe_2$). In the $Pr_{16}Fe_{76}B_8$ magnets three phases have been identified: $Pr_2Fe_{14}B$ (Φ), Pr rich and $Pr_{1+\varepsilon}Fe_4B_4$ (η). Good magnetic properties have been achieved in the $Pr_{16}Fe_{76}B_8$ magnet produced using a fine powder milled for 18 hours (B_r = 1.19 T and $\mu_{0i}H_c$ = 1.44 T). For the $Pr_{17}Fe_{79}B_4$ magnet a longer milling time has been necessary to improve the magnetic properties (B_r = 1.14 T and $\mu_{0i}H_c$ = 1.16T). In this case remanence and coercivity were slightly lower than that obtained in former due to the low boron content in the alloy (4 at.%).

Introduction

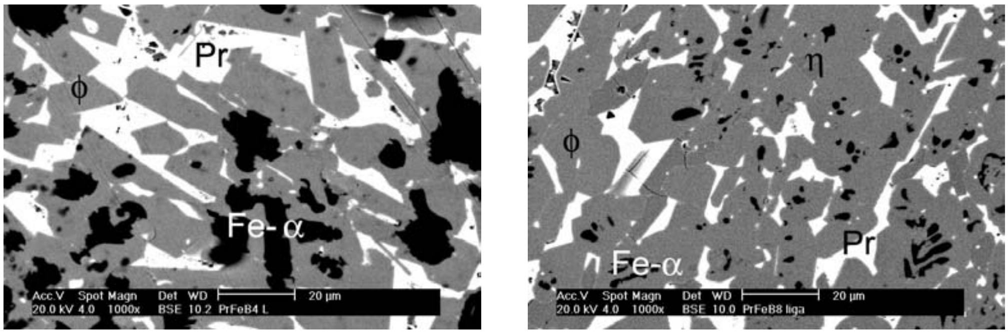
The influence of milling step on the magnetic properties and microstructures of rare earth-iron-boron-type magnets (RE = Nd and Pr) have been studied by various authors [1-3]. Particle size after milling and grain size after sintering are very important interdependent factors for controlling the microstructure and, hence, the magnetic properties of the sintered magnets. Recently, a new powder transfer technique has been developed for production of such magnets in a laboratory scale [4,5]. Nd and Pr- based magnets were successfully produced using various milling times and this low-cost technique. In this work the microstructures and mean grain size of the Pr-based HD magnets have been investigated.

Experimental procedure

Commercially available $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$ alloys were processed in the as-cast state (ingot broken pieces). The processing conditions and magnetic properties of these HD magnets have been reported previously [5]. The microstructural and microanalysis characterization of the alloys and magnets were carried out using a scanning electron microscope fitted with energy dispersive X-ray analysis. Grain size measurements were carried out using optical microscope fitted with an image analyzer. Samples were etched with nital (3%) in order to reveal the grain boundaries for measurement of the mean grain size.

Results and discussion

The microstructures of the $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$ as-cast alloys are shown in Fig. 1a and b, respectively. The $Pr_{17}Fe_{79}B_4$ alloy is composed of the matrix phase $Pr_2Fe_{14}B$ (ϕ), praseodymium-rich phase and α-Fe (free-iron). The $Pr_{16}Fe_{76}B_8$ alloy is also composed by same phases identified in the former with an extra boron-rich phase ($Pr_{1+\varepsilon}Fe_4B_4$ or η). Various works reported these typical phases in sintered magnets [6-12]. A comparison between these two microstructures shows that the alloy with high boron content has a somewhat more refined structure.



(a) (b)

Fig. 1. Microstructures of as-cast alloys: a) $Pr_{17}Fe_{79}B_4$ and b) $Pr_{16}Fe_{76}B_8$; (1000x).

The chemical composition of the phases determined by EDX on a SEM for as-cast alloys $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$ are given in Table 1. The matrix phase $Pr_2Fe_{14}B$ (ϕ) and boron rich $Pr_{1+\varepsilon}Fe_4B_4$ (η) were identified by Fe:Pr ratio [13]. Both phases, $Pr_{1+\varepsilon}Fe_4B_4$ and α-Fe, are detrimental to the magnetic properties of the sintered magnet. The magnetic properties of HD sintered magnets prepared from the $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$ alloys are given in Tables 2 and 3, respectively.

The microstructures of the HD sintered magnets prepared from as-cast alloys employing various milling times are shown in Fig. 2 (a-d and a'-d'). The phases found are identified in the micrographies.

Table 1 – Composition determined by EDX of phases present at as-cast alloys $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$.

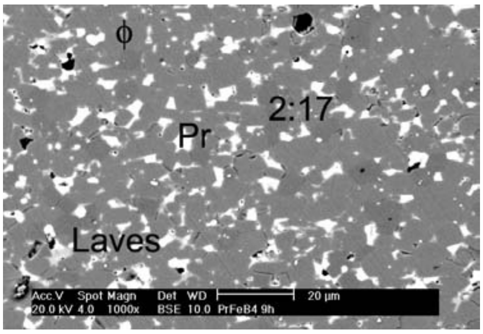
Alloy	Phase	Chemical composition (at.%)	
		Pr	Fe
$Pr_{17}Fe_{79}B_4$	$Pr_2Fe_{14}B$ (ϕ)	13.9±0.3	86.1±1.7
	Pr rich	94.4±1.8	5.6±0.1
	α-Fe	1.2±0.03	98.8±2.0
$Pr_{16}Fe_{76}B_8$	$Pr_2Fe_{14}B$ (ϕ)	13.4±0.3	86.6±1.7
	$Pr_{1+\varepsilon}Fe_4B_4$ (η)	24.9±0.5	75.1±1.5
	Pr rich	83.3±1.6	12.5±0.3
	α-Fe	1.1±0.03	98.9±2.0

Table 2 – Magnetic properties of $Pr_{17}Fe_{79}B_4$ HD sintered magnets produced from the as-cast alloy using various milling times [5].

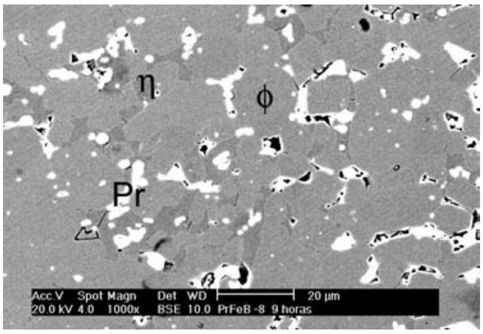
Milling time (h)	B_r (T)	$\mu_{0\,i}H_c$ (T)	$\mu_{0\,b}H_c$ (T)	$(BH)_{max.}$ (kJ/m^3)	SF	ρ (g/cm^3)
9	1.05	1.03	0.78	167	0.42	6.15
18	1.06	1.06	0.83	197	0.60	7.33
27	1.14	1.16	0.93	217	0.61	7.35
36	1.04	1.12	0.81	175	0.36	7.37

Table 3 – Magnetic properties of $Pr_{16}Fe_{76}B_8$ HD sintered magnets produced from the as-cast alloy using various milling times [5].

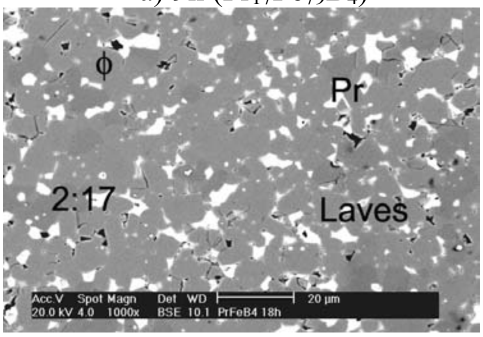
Milling time (h)	B_r (T)	$\mu_{0\,i}H_c$ (T)	$\mu_{0\,b}H_c$ (T)	$(BH)_{max.}$ (kJ/m^3)	SF	ρ (g/cm^3)
9	1.02	1.00	0.79	197	0.64	7.28
18	1.19	1.44	1.08	280	0.78	7.33
27	0.95	1.50	0.85	158	0.63	7.37
36	0.92	1.37	0.81	151	0.53	7.32



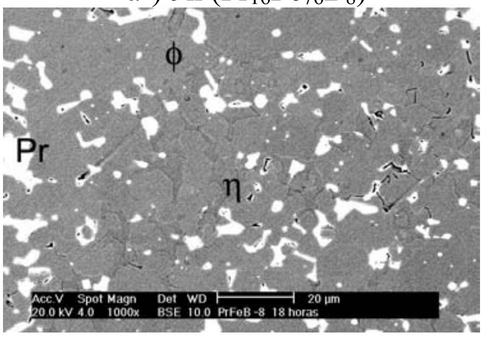
a) 9h ($Pr_{17}Fe_{79}B_4$)



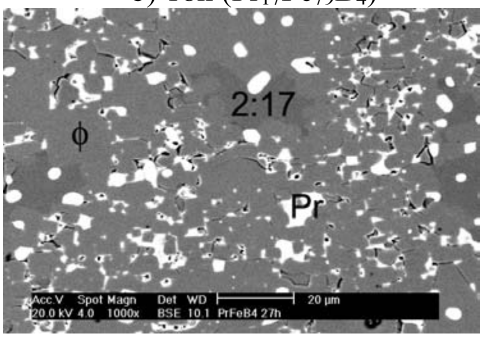
a') 9h ($Pr_{16}Fe_{76}B_8$)



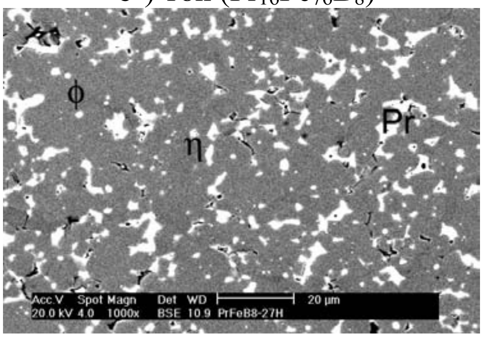
b) 18h ($Pr_{17}Fe_{79}B_4$)



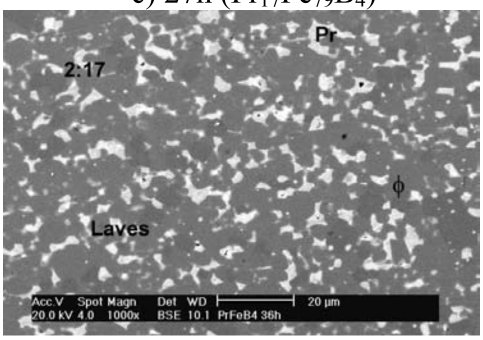
b') 18h ($Pr_{16}Fe_{76}B_8$)



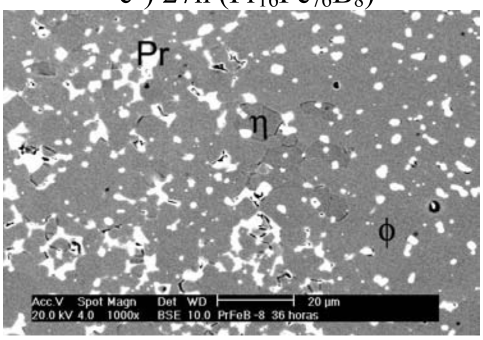
c) 27h ($Pr_{17}Fe_{79}B_4$)



c') 27h ($Pr_{16}Fe_{76}B_8$)



d) 36h ($Pr_{17}Fe_{79}B_4$)



d') 36h ($Pr_{16}Fe_{76}B_8$)

Fig. 2 – Micrographies of the $Pr_{17}Fe_{79}B_4$ HD sintered magnets (a-d) and for the $Pr_{16}Fe_{76}B_8$ HD magnets (a'-d'), milling time: 9, 18, 27 e 36 hours; (1000x).

The chemical composition the phases determined by EDX in the HD sintered magnets prepared from the $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$ alloys are given in Table 4 and 5. Boron cannot be analyzed by EDX and the phase were identified using Fe:Pr ratio [13].

In the magnets prepared using the $Pr_{17}Fe_{79}B_4$ alloy were identified the matrix phase (ϕ), the Pr rich in the grain boundaries of the matrix phase, the phase Pr_2Fe_{17} and the Laves Phase $PrFe_2$. The Pr_2Fe_{17} phase is deleterious for magnetic properties because it causes reversal magnetization and diminution of the intrinsic coercivity in the sintered magnets. This phase is localized inside of the matrix phase and was not identified in the $Pr_{17}Fe_{79}B_4$ alloy (Fig. 1 a). This phase is present only in permanent magnets prepared using alloys with less than 5% at. B [14-16]. Low boron content promotes the formation of the phase Pr_2Fe_{17} and this inhibits the growing of the matrix phase [14]. The Laves phase, $PrFe_2$, is found in the grain boundary of matrix phase together with the Pr-rich phase.

In the HD sintered magnets prepared from alloy $Pr_{16}Fe_{76}B_8$ three phases were identified: the $Pr_2Fe_{14}B$ matrix phase (ϕ), Pr-rich and B-rich phases ($Pr_{1+\varepsilon}Fe_4B_4$). The boron-rich phase is invariably found in magnets with B-content superior to 5% at.

Table 4. Chemical composition determined by EDX for the phases present on the $Pr_{17}Fe_{79}B_4$ magnets.

Milling time (h)	Phase	Chemical composition (at %)	
		Pr	Fe
9	$Pr_2Fe_{14}B$ (ϕ)	13.4±0.3	86.6±1.7
	Pr_2Fe_{17}	11.6±0.2	88.4±1.8
	Pr rich	89.8±1.8	10.2±0.2
	Laves	32.1±0.6	67.9±1.3
18	$Pr_2Fe_{14}B$ (ϕ)	13.3±0.3	86.7±1.7
	Pr_2Fe_{17}	11.5±0.2	88.5±1.8
	Pr rich	89.0±1.8	11.0±0.2
	Laves	23.4±0.5	76.6±1.5
27	$Pr_2Fe_{14}B$ (ϕ)	13.3±0.3	86.7±1.7
	Pr_2Fe_{17}	11.5±0.2	88.5±1.8
	Pr rich	89.7±1.8	10.3±0.2
	Laves	22.1±0.5	77.9±1.5
36	$Pr_2Fe_{14}B$ (ϕ)	13.3±0.3	86.7±1.7
	Pr_2Fe_{17}	11.6±0.2	88.4±1.8
	Pr rich	89.9±1.8	10.1±0.2
	Laves	22.3±0.5	77.7±1.5

Table 5. Chemical composition determined by EDX for the phases present on the $Pr_{16}Fe_{76}B_8$ magnets.

Milling time (h)	Phase	Chemical composition (at.%) Pr	Fe
9	$Pr_2Fe_{14}B$ (ϕ)	14.4±0.3	85.6±1.7
	$Pr_{1+\varepsilon}Fe_4B_4$ (η)	24.6±0.5	75.4±1.5
	Pr rich	88.1±1.7	11.9±0.2
18	$Pr_2Fe_{14}B$ (ϕ)	14.2±0.3	85.8±1.7
	$Pr_{1+\varepsilon}Fe_4B_4$ (η)	26.0±0.5	74.0±1.5
	Pr rich	87.8±1.7	12.2±0.3
27	$Pr_2Fe_{14}B$ (ϕ)	14.7±0.3	85.3±1.7
	$Pr_{1+\varepsilon}Fe_4B_4$ (η)	24.7±0.5	75.3±1.5
	Pr rich	88.0±1.7	12.0±0.2
36	$Pr_2Fe_{14}B$ (ϕ)	14.3±0.3	85.1±1.7
	$Pr_{1+\varepsilon}Fe_4B_4$ (η)	23.6±0.5	76.4±1.5
	Pr rich	85.4±1.6	14.6±0.4

Fig. 3 shows the mean grain size analyzed using an image analyzer. The mean grain size decreases with increasing milling time and the best magnetic properties were obtained in 27 and 18 hours for the magnets prepared from $Pr_{17}Fe_{79}B_4$ e $Pr_{16}Fe_{76}B_8$ alloys, respectively. In general the grain size is smaller for the sintered magnets prepared with $Pr_{17}Fe_{79}B_4$ alloy. This has been attributed to the presence of the Pr_2Fe_{17} phase. It is believed that this phase inhibit the matrix phase growth during the sintering [14]. Prolonged milling times diminished the magnetic properties for magnets prepared with both alloys. This has been attributed previously to superficial oxidation and crystal structure defects [2,17,18].

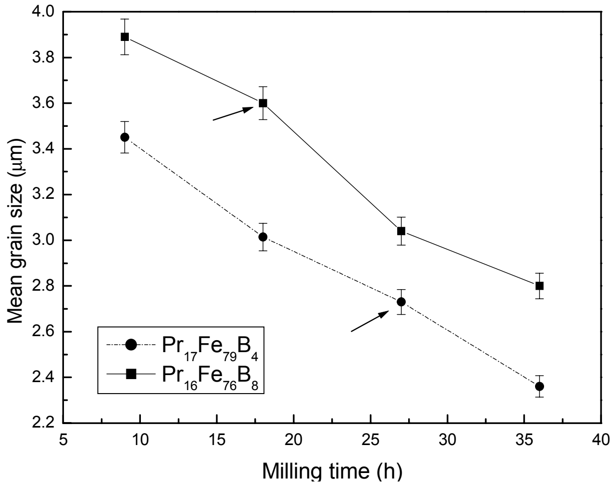


Fig. 3 – Mean grain size versus milling time for the HD sintered magnets prepared with the $Pr_{17}Fe_{79}B_4$ and $Pr_{16}Fe_{76}B_8$ alloys. The arrows indicate the magnets with best magnetic properties.

Conclusions

It has been shown that the Pr_2Fe_{17} phase causes a decrease in the mean grain size of the HD sintered magnets prepared with $Pr_{17}Fe_{79}B_4$ alloy (compared to that of magnets prepared with $Pr_{16}Fe_{76}B_8$ alloy). The presence of the Pr_2Fe_{17} and $PrFe_2$ phases at $Pr_{17}Fe_{79}B_4$ magnets was more deleterious to the magnetic properties than the presence of the B-rich phases ($Pr_{1+\varepsilon}Fe_4B_4$) in the $Pr_{16}Fe_{76}B_8$ sintered magnets. Prolonged milling times were not beneficial to improve the magnetic properties of the sintered magnets prepared with both alloys.

Acknowledgments

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