

A Comparative Study Between Low and High-Energy Milling Processes for the Production of HD PrFeCoBNb Sintered Magnets

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Keywords: High-energy milling, hydrogen decrepitation, PrFeB sintered magnets.

Abstract. Roller-ball milling (RBM) or planetary ball milling (PBM) have been used together with the hydrogen decrepitation (HD) process to produce sintered permanent magnets based on a mixture of Pr₁₆Fe₇₆B₈ and Pr_{14.00}Fe_{63.90}Co_{16.00}B_{6.00}Nb_{0.10} magnetic alloys. Five distinct compositions have been studied comparing low- and high-energy milling. Magnets with a particular composition and prepared using these two routes exhibited similar magnetic properties. Modifications have been carried out in the procedure of the HD stage for PBM in order to guarantee a high degree of crystallographic alignment. Pr_{15.00}Fe_{69.95}Co_{8.00}B_{7.00}Nb_{0.05} magnets showed the best maximum energy product for both processing routes (~ 247 kJm⁻³). A significant reduction in the milling time (93%) has been achieved with high-energy processing, the greatest advantage over the low-energy route.

Introduction

The mixture of cast alloys is an effective way to produce Pr-based magnets with distinct compositions from the raw material using roller ball milling (RBM) [1]. However, RBM is an expensive step since it responds for two-thirds of the whole processing time of sintered magnets. High-energy milling (HEM) has become an important tool for research on powder metallurgy due to possibility to reduce drastically time processing. Another important feature of the HEM is the preparation of new materials by mechanical alloying [2].

Recently Pr₁₆Fe₇₆B₈ sintered magnets have been produced by planetary ball milling (PBM) and the magnetic properties obtained have been very similar to those achieved by RBM [3]. However, it was necessary to reduce the hydrogen decrepitation (HD) process time in 96% to guarantee a high crystallographic alignment of the Pr₂Fe₁₄B phase [3].

The mixture of alloys exposed for a short period of time to H₂ and subsequently milled by PBM is still not evaluated and alloys with different compositions may absorb distinct amounts of hydrogen and influence magnetic properties. This paper addresses this aspect and the following section reports the experimental setup utilized to prepare the sintered magnets. Next, magnetic and microstructural results are presented and discussed. The fourth section reports the conclusions and the last section lists the references.

Experimental Setup

Table 1 reports the compositions evaluated with the mixture in % wt. of Pr₁₆Fe₇₆B₈ (in the as-cast state) and Pr_{14.00}Fe_{63.90}Co_{16.00}B_{6.00}Nb_{0.10} (annealed during 72.0ks at 1273K) magnetic alloys. Fig. 1 presents the processing route utilized. Metallographic characterization has been carried out using scanning electron microscopy (SEM). X-ray diffraction (XRD) has been employed to determine the crystallographic alignment of magnets by an alternative method recently reported [4]. It has been used CuK α radiation and 2 θ was varied between 20-80° at a scanning rate of 1°min⁻¹.

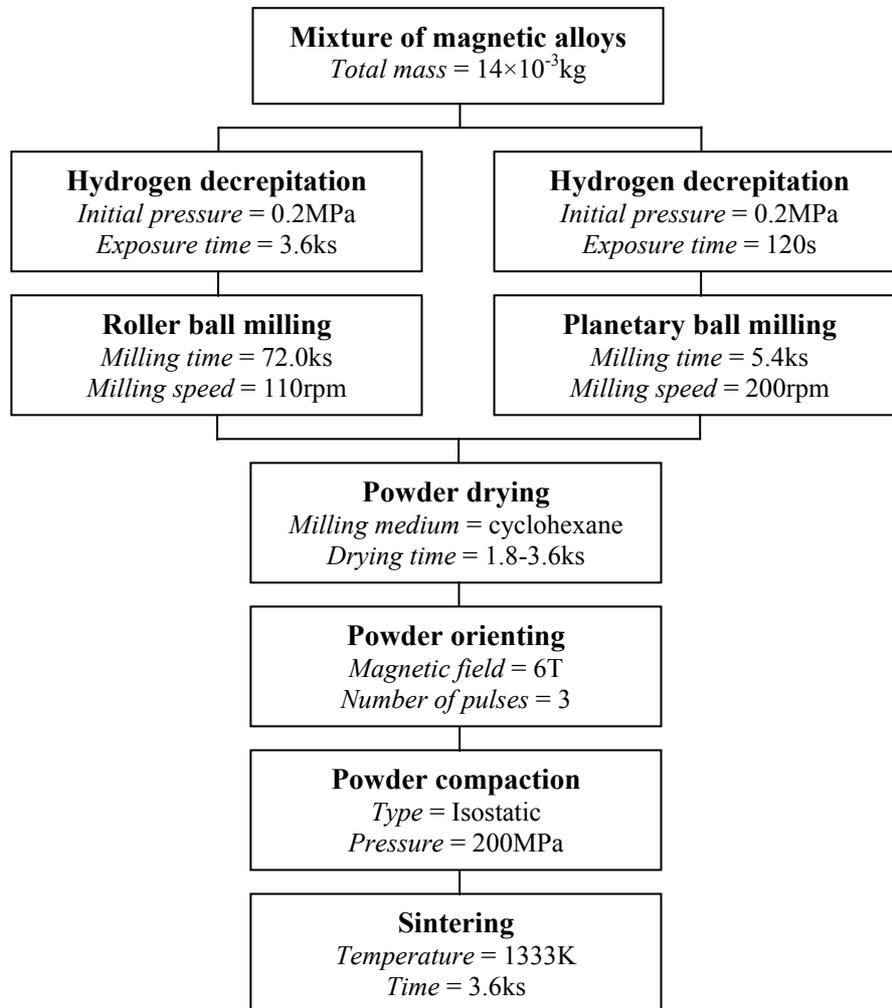


Figure 1 – Processing route used for the production of the PrFeCoBNb sintered magnets.

Table 1 – Compositions evaluated from the mixture of magnetic alloys.

Alloys	Proportion of Mixture (% wt.)	Final Composition
Pr _{14.00} Fe _{63.90} Co _{16.00} B _{6.00} Nb _{0.10} Pr ₁₆ Fe ₇₆ B ₈	75.0	Pr _{14.50} Fe _{66.92} Co _{12.00} B _{6.50} Nb _{0.08}
	25.0	
	62.5	Pr _{14.75} Fe _{68.44} Co _{10.00} B _{6.75} Nb _{0.06}
	37.5	
	50.0	
	50.0	Pr _{15.00} Fe _{69.95} Co _{8.00} B _{7.00} Nb _{0.05}
	37.5	
	62.5	
25.0	Pr _{15.25} Fe _{71.46} Co _{6.00} B _{7.25} Nb _{0.04}	
75.0		
		Pr _{15.50} Fe _{72.98} Co _{4.00} B _{7.50} Nb _{0.02}

Results and discussion

Fig. 2 shows the variation of remanence, intrinsic coercivity and maximum energy product with the Pr content. In general, RBM and PBM provided values of B_r similar for each pair of magnets of a given composition, considering the limits of the experimental error. Remanence is expressed mathematically by [5-6]

$$B_r = P f J_s \langle \cos \Theta \rangle, \quad (1)$$

where P is the packing factor (ratio measured density to the theoretical density of a magnet) and f , J_s and $\langle \cos \Theta \rangle$ are the volumetric fraction, polarization saturation and degree of crystallographic alignment of the magnetic phase, respectively. J_s and f must be considered constant for magnets of same composition. Consequently, P and $\langle \cos \Theta \rangle$ should have compensated each other in the same proportion. The hydrostatic density of all samples ranged between (7.47 ± 0.04) and $(7.55 \pm 0.04) \text{gcm}^{-3}$, influencing P less than 2%. The $\langle \cos \Theta \rangle$ index has been quantified for the $\text{Pr}_{15.00}\text{Fe}_{69.95}\text{Co}_{8.00}\text{B}_{7.00}\text{Nb}_{0.05}$ sintered magnets, which presented the highest $(\text{BH})_{\text{max}}$. XRD patterns of magnets prepared for both milling processes are showed in Fig. 3. The intensities of the $\text{Pr}_2(\text{Fe,Co})_{14}\text{B}$ phase planes are quite similar for both cases. The magnetic alignment is (0.90 ± 0.02) and (0.88 ± 0.02) for RBM and PBM magnets, respectively. These values are comparable to that previously reported for $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$ magnets which employed the same processing route [3].

PBM have provided better values of $\mu_0 H_c$ than RBM. This has been ascribed to microstructural changes of the magnets, which will be discussed below. From the $\text{Pr}_{14.75}\text{Fe}_{68.44}\text{Co}_{10.00}\text{B}_{6.75}\text{Nb}_{0.06}$ composition onwards, a tendency of equality with a slightly raise of the intrinsic coercivity using both milling processes has been verified. Increasing the Pr content, a better insulation between the hard magnetic grains of the matrix phase is achieved due to a larger amount of the intergranular Pr-rich phase and, consequently, higher values of $\mu_0 H_c$ are expected. $(\text{BH})_{\text{max}}$ presented the same behavior than that presented by remanence due to its directly proportional dependence on this property.

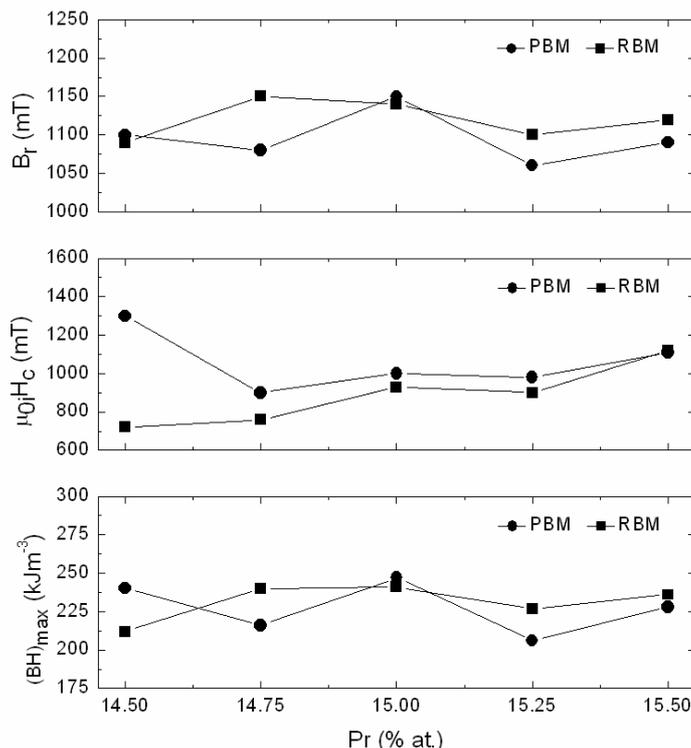


Figure 2 – Variation of B_r , $\mu_0 i H_c$ and $(BH)_{max}$ with the praseodymium content. Error: $\pm 2\%$.

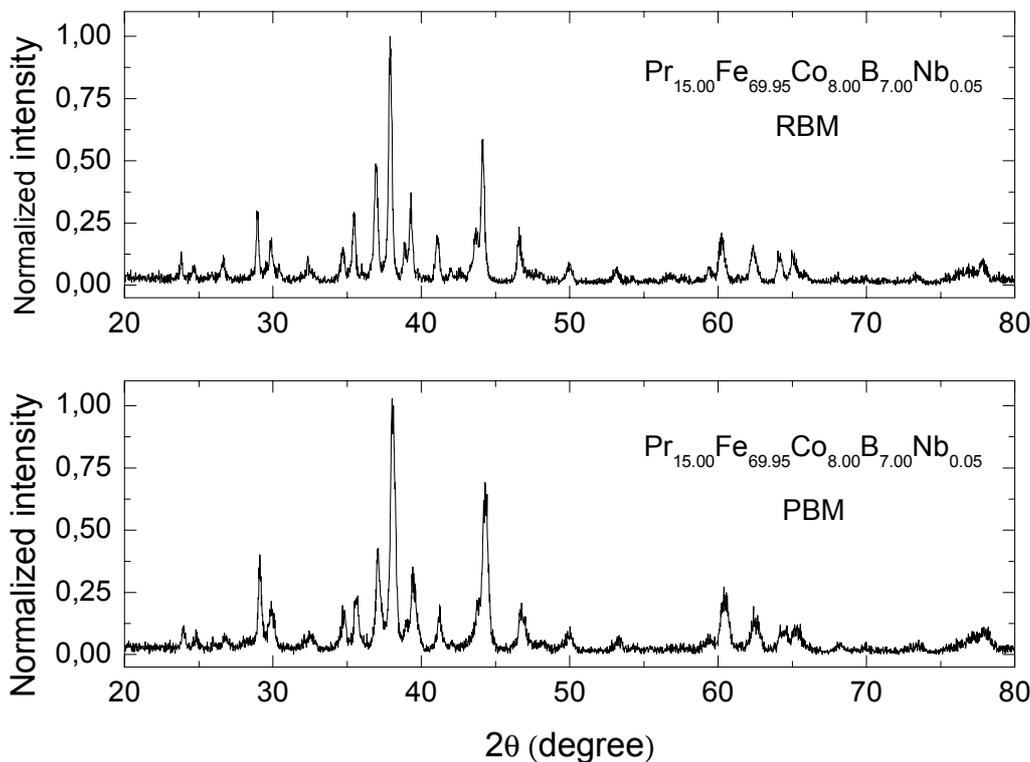


Figure 2 – X-ray diffraction patterns of the $\text{Pr}_{15.00}\text{Fe}_{69.95}\text{Co}_{8.00}\text{B}_{7.00}\text{Nb}_{0.05}$ sintered magnets prepared by RBM and PBM.

Three phases have been identified in all magnets: $\text{Pr}_2(\text{Fe},\text{Co})_{14}\text{B}$ (Φ – matrix), $\text{Pr}_3(\text{Fe},\text{Co})$ (Pr-rich) and $\text{Pr}_{1+\epsilon}(\text{Fe},\text{Co})_4\text{B}_4$ (boron-rich), common for both magnetic alloys utilized in the mixture to prepare the sintered magnets (obviously the $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$ alloy does not present cobalt in these phases). A fourth phase, $\text{Pr}(\text{Fe},\text{Co})_2$ (Laves phase), has been found in $\text{Pr}_{14.50}\text{Fe}_{66.92}\text{Co}_{12.00}\text{B}_{6.50}\text{Nb}_{0.08}$

and $\text{Pr}_{14.75}\text{Fe}_{68.44}\text{Co}_{10.00}\text{B}_{6.75}\text{Nb}_{0.06}$ compositions. It comes from the $\text{Pr}_{14.00}\text{Fe}_{63.90}\text{Co}_{16.00}\text{B}_{6.00}\text{Nb}_{0.10}$ alloy, which presents a volumetric fraction of 2.5% of $\text{Pr}(\text{Fe},\text{Co})_2$ according to Barbosa [7-8]. From the $\text{Pr}_{15.00}\text{Fe}_{69.95}\text{Co}_{8.00}\text{B}_{7.00}\text{Nb}_{0.05}$ composition, probably due to the dilution of the cobalt content in the magnet, it has not been found.

It has been verified that the composition of the Φ phase depends on the mixture of $\text{Pr}_{14.00}\text{Fe}_{63.90}\text{Co}_{16.00}\text{B}_{6.00}\text{Nb}_{0.10}$ and $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$ alloys. Table 2 reports the composition of the $\text{Pr}_2(\text{Fe},\text{Co})_{14}\text{B}$ phase for each magnet prepared. Since Co and Fe present similar atomic radius and electronegativity, the former substitutes the latter. However, the ratio % at. of Pr to the % at. of (Fe+Co) keeps practically unchanged, around 0.16. It means that there is one Pr atom for each 6.25 atoms of Fe plus Co, close to the theoretical value (1:7).

The microstructures of the $\text{Pr}_{15.00}\text{Fe}_{69.95}\text{Co}_{8.00}\text{B}_{7.00}\text{Nb}_{0.05}$ sintered magnets prepared using RBM and PBM are showed in Fig. 3 ((a)-(d)). The Pr-rich phase for the magnet prepared from PBM present smaller areas compared to the RBM magnet. Besides, the distribution of the Pr-rich phase in the PBM magnet is more homogeneous, which favors intrinsic coercivity. Smaller mean grain sizes (MGS) have been obtained with PBM for all compositions prepared, as also listed in Table 2. With the experimental conditions utilized, PBM has provided a more homogenous MGS than RBM, evidenced by the standard deviation.

No phase transformations have been verified with the PBM (considering the experimental conditions utilized) or even contaminations from the milling balls or jar.

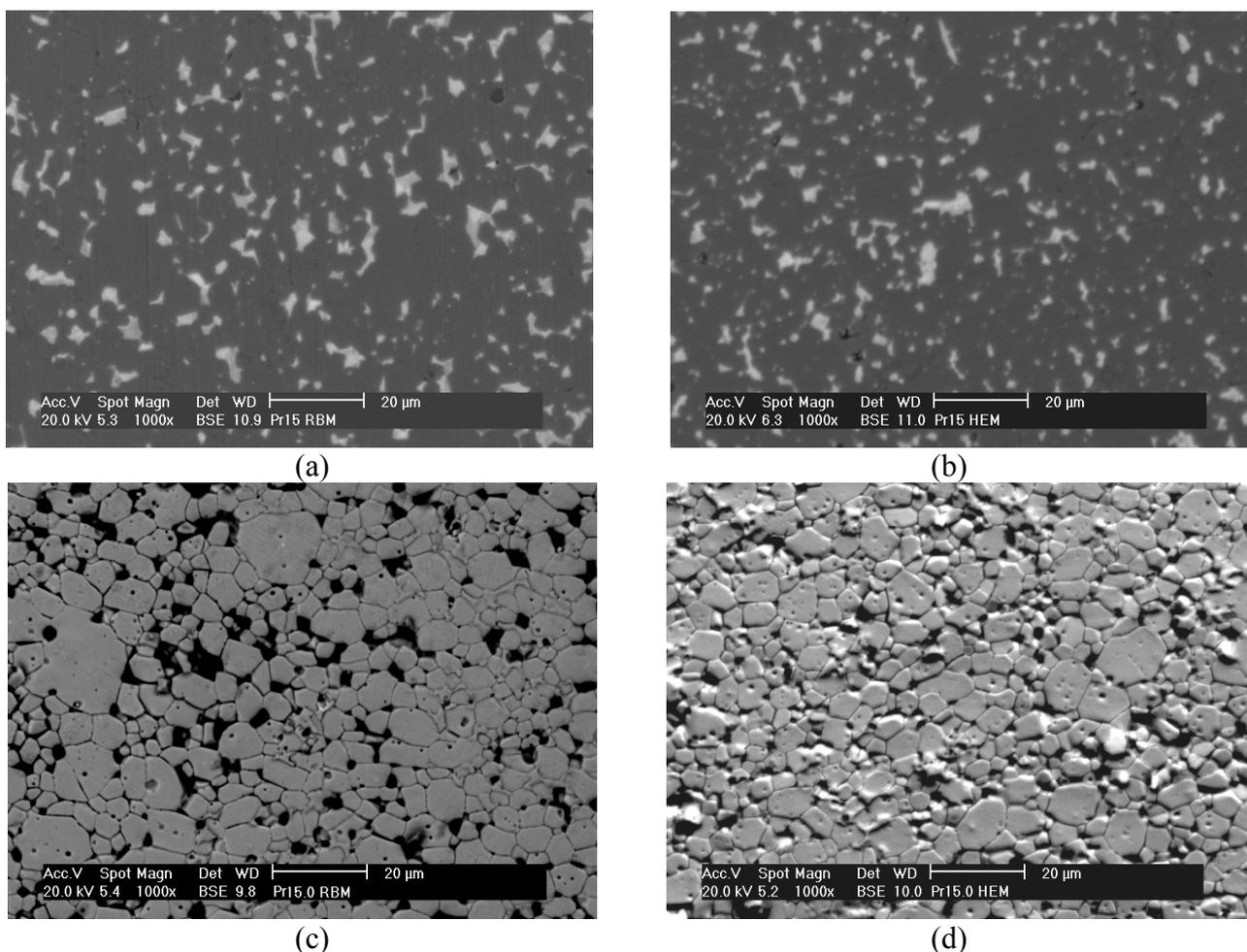


Figure 3 – Microstructures of the $\text{Pr}_{15.00}\text{Fe}_{69.95}\text{Co}_{8.00}\text{B}_{7.00}\text{Nb}_{0.05}$ sintered magnets prepared using RBM and PBM. In the boundary grains of the etched samples, the secondary phase is $\text{Pr}_{1+\epsilon}(\text{Fe},\text{Co})_4\text{B}_4$.

Table 2 – Mean grain size, standard deviation and composition of the Pr₂(Fe, Co)₁₄B phase. Boron is not presented.

Nominal composition of the mixture	Milling process	MGS (µm)	σ (µm)	Pr (%at.)	Fe (%at.)	Co (%at.)
Pr _{14.50} Fe _{66.92} Co _{12.00} B _{6.50} Nb _{0.0} 8	RBM	3.64	1.87	13.35	73.25	13.14
	PBM	3.26	1.49	14.12	74.09	11.51
Pr _{14.75} Fe _{68.44} Co _{10.00} B _{6.75} Nb _{0.0} 6	RBM	3.53	1.83	13.44	76.04	10.16
	PBM	3.42	1.65	13.26	75.99	10.44
Pr _{15.00} Fe _{69.95} Co _{8.00} B _{7.00} Nb _{0.05}	RBM	4.49	2.05	13.38	77.18	9.12
	PBM	4.23	2.11	13.01	77.05	9.67
Pr _{15.25} Fe _{71.46} Co _{6.00} B _{7.25} Nb _{0.04}	RBM	4.09	1.67	13.14	79.98	6.56
	PBM	4.07	2.15	13.12	79.55	7.04
Pr _{15.50} Fe _{72.98} Co _{4.00} B _{7.50} Nb _{0.02}	RBM	4.33	2.00	13.92	80.75	4.90
	PBM	3.90	1.84	13.18	80.66	5.71

Summary

Sintered permanent magnets have been prepared from the mixture of Pr_{14.00}Fe_{63.90}Co_{16.00}B_{6.00}Nb_{0.10} and Pr₁₆Fe₇₆B₈ magnetic alloys using roller ball milling and planetary ball milling. RBM and PBM provided values of B_r similar for each pair of magnets of a given composition, considering the limits of the experimental error. PBM have provided better values of μ₀iH_c than RBM. Pr_{15.00}Fe_{69.95}Co_{8.00}B_{7.00}Nb_{0.05} magnets showed the best maximum energy product for both processing routes (~ 247 kJm⁻³). Planetary ball milling has provided a more homogeneous microstructure than roller ball milling.

Acknowledgments

The authors thank IPEN-CNEN by facilities and FAPESP for the financial support of this investigation and for the provision of a research grant (E. A. Périgo, contract number 2005/04711-2).

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