A STUDY OF HIGH-ENERGY MILLING FOR THE PRODUCTION OF SINTERED PrFeB MAGNETS

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ABSTRACT

Sintered $Pr_{16}Fe_{76}B_8$ magnets have been produced using the hydrogen decrepitation (HD) process and high-energy planetary ball milling. Investigations have been carried out to evaluate the influence of the milling speed and time. The best magnetic properties obtained were: B_r = (1020 ± 2) mT, $\mu_{0i}H_c$ = (1420 ± 3) mT and $(BH)_{max}$ = (200 ± 4) kJm^{-3}, for a magnet prepared with the alloy milled at 200 rpm for 4.5 kiloseconds (ks). Magnets prepared from this powder exhibited a superior intrinsic coercivity (at least 10% higher) compared to that of magnets produced using low-energy ball milling. However, the remanence and energy product of the latter were somewhat lower. It has been inferred that this is a feature of high-energy milling. Another important feature of the high-energy milling was the dramatic reduction in the processing time (about 90%). Microstructural observation have shown that increasing the milling time and keeping constant the rotational mill speed caused an exponential grain size reduction in the sintered magnet. Increasing the milling speed also reduced the grain size and influenced both remanence and intrinsic coercivity.

Key-words: Hydrogen decrepitation, high-energy milling, PrFeB.

INTRODUCTION

The production of REFeB (RE = Pr, Nd) sintered magnets involves a multistep process [(1)]. It is possible to identify at least seven steps: melting of the alloy, homogenization, milling, powder magnetic alignment and compaction, sintering and post-sintering heat treatment. Milling is time consuming, even using the hydrogen decrepitation (HD) process. Good HD sintered REFeB magnets have been produced using the "roller" ball milling (RBM) from alloys comminuted between 64.8 and 72.0 ks (18 and 20 hours, respectively)[(2-3)]. If production costs are considered, reducing the processing time is essential, without changing significantly the magnetic properties. This paper addresses this aspect and reports work carried out to produce PrFeB sintered magnets from HD powders milled for a short time using high-energy milling.

EXPERIMENTAL

A commercial $Pr_{16}Fe_{76}B_8$ (wt%: 34.24Pr - 64.45Fe - 1.31B) alloy in the as-cast state was used in this study. To produce the sintered Pr-based magnets using the HD process, 0.014 kg (14 g) of the bulk ingot was placed in a stainless steel hydrogenation vessel which was evacuated to backing-pump pressure. Hydrogen was then introduced to a pressure of 2 bar which resulted in decrepitation of the bulk material. The decrepitated hydride material was transferred to a planetary ball mill and milled for several rotational speeds and times (150 to 300 rpm with steps of 50 rpm, milling time from 1.8 to 5.4 ks with steps of 0.9 ks) using cyclohexane as the milling medium. A preliminary evaluation showed that hydrogen is not an effective milling atmosphere due to the formation of agglomerates. Ball-to-powder weight ratio was kept constant for all experiments (10:1). The resultant pyrophoric powder was dried for 1.5 ks and transferred to a small cylindrical rubber tube under a nitrogen atmosphere. The resultant fine powder was then pulsed at a magnetic field of 6T, isostatically pressed at 200 MPa and vaccum sintered at 1333 K for 3.6 ks (60 min) and furnace cooled.

Magnetic characterization of the HD sintered $Pr_{16}Fe_{76}B_8$ permanent magnets was carried out using a permeameter. Remanence (B_r), intrinsic coercivity ($\mu_{0i}H_c$) and maximum energy product ($(BH)_{max}$) have been obtained from the second quadrant hysteresis curve. Microstructural observations were carried out using a scanning electron microscope. Grain size measurements were carried out using image analysis. Samples for grain analysis were etched with a solution of 25%H_2O - 50%HCl - 25%HNO_3 (%vol.) in order to reveal the grain boundaries.

Milling times longer than 5.4 ks were not practical due to difficulty to handle the extremely fine pyrophoric powder. On the other hand, it was verified that speeds below 150 rpm yield a coarse powder, useless to produce good sintered REFeB magnets. No contamination has been found in any sample from the milling spheres or jar. Based on the magnetic properties obtained from the hydrogen decrepitated $Pr_{16}Fe_{76}B_8$ alloy milled for 1.8 and 2.7 ks, samples produced with longer times were investigated only for the speed of 200 rpm.

RESULTS AND DISCUSSION

The magnetic properties for the magnets produced from the alloy hydrogen decrepitated and milled for 1.8 ks (30 min) are showed in Figure 1. Remanence reached a peak of 860 mT for a milling speed of 200 rpm. The improvement in B_r with the milling speed has been attributed to better alignment degree of the $Pr_2Fe_{14}B$ (ϕ) grains. Rotational milling speed superior to 200 rpm diminished the remanence, possibly due to formation of agglomerattes of the fine powder. The magnet produced using a milling speed of 300 rpm showed the best $\mu_{0i}H_c$. This has been attributed to a smaller grain size obtained at higher speeds. Figure 2 shows the magnet grain size as a function of the rotational milling speed. It has also been verified that low milling times led to heterogeneities of particle size (even at high speeds). In this case, the magnet exhibits very small grains (3 μm) and also large grains (~ 45 μm). This effect is clearly seen in Figure 3 (a) and most certainly influence the remanence since larger grains have a multi-domain structure.

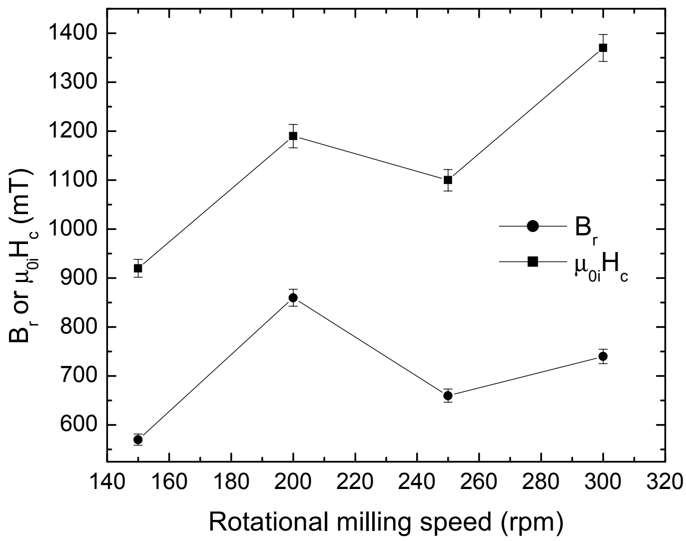


Figure 1 – Variation of remanence and intrinsic coercivity with milling speed from $Pr_{16}Fe_{76}B_8$ alloy milled for 1.8 ks.

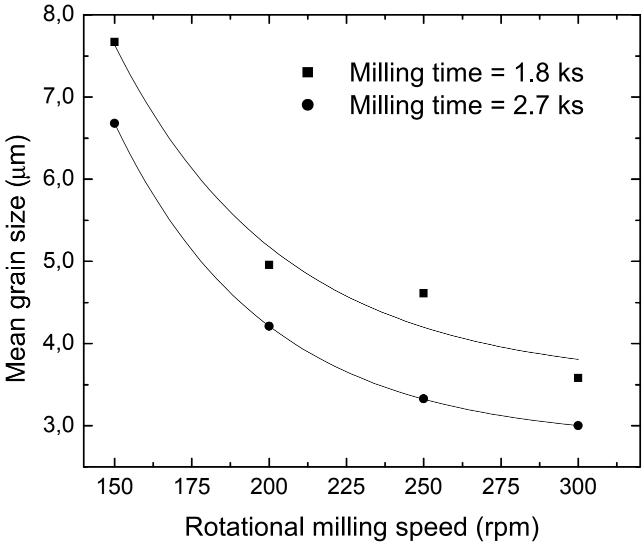
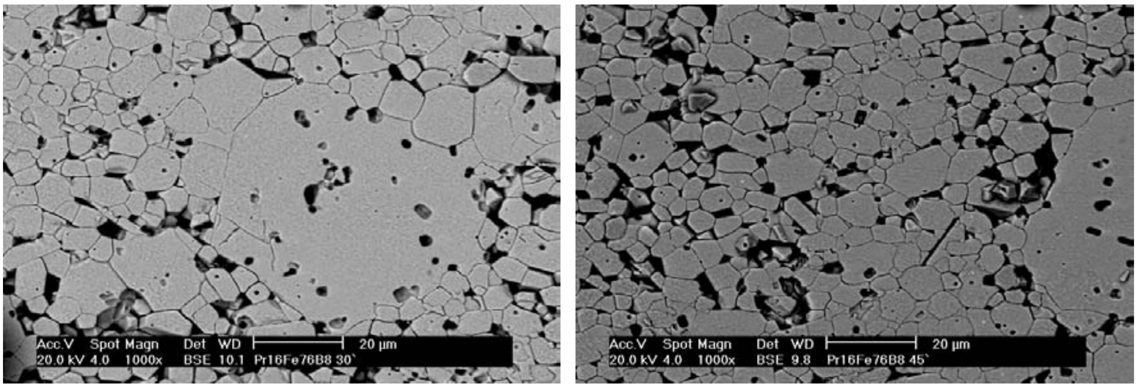


Figure 2 – Variation of mean grain size with milling speed from $Pr_{16}Fe_{76}B_8$ alloy milled for 1.8 and 2.7 ks.



(a) (b)

Figure 3 – General view of the microstructure of $Pr_{16}Fe_{76}B_8$ magnet produced from the decrepitated ingot milled at 200 rpm for (a) 1.8 and (b) 2.7 ks.

Figure 4 shows the variation of the magnetic properties with milling speed for magnets produced using a constant milling time of 2.7 ks (45 min). Again, the better remanence and energy product were obtained for the sintered magnet milled at 200 rpm. The best $\mu_{0i}H_c$ was obtained for the magnet prepared from the alloy milled at 250 rpm, although the intrinsic coercivity for the alloy milled at 300 rpm is quite similar. It can be observed in Figure 3 (b) a reduction of the mean grain size (about 15%) compared to the previous case (Figure 2). However, the heterogeneity of the microstructure is very evident.

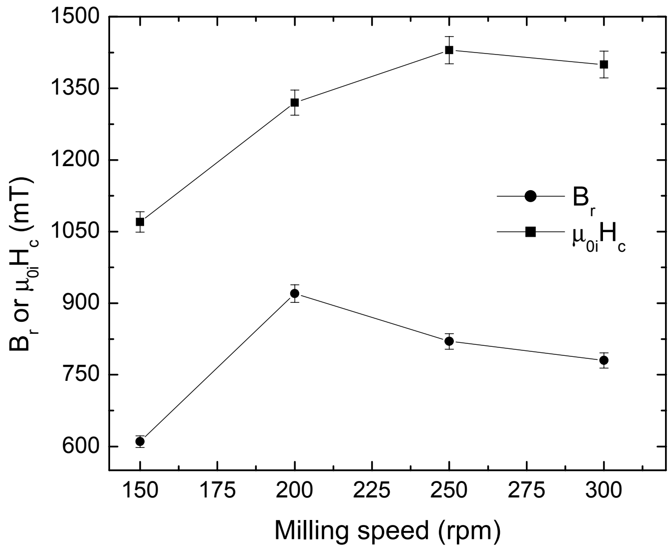


Figure 4 – Variation of remanence and intrinsic coercivity with milling speed from $Pr_{16}Fe_{76}B_8$ alloy milled for 2.7 ks.

The magnetic properties for the $Pr_{16}Fe_{76}B_8$ magnet prepared from the decrepitated alloy milled for 3.6 ks (60 min) are presented in Figure 5. There was a steady improvement in remanence up to 4.5 ks. The intrinsic coercivity showed a gradual improvement followed by a slight decrease. It was verified that the mean grain size also reduced with longer milling time, improving the homogeneity of the microstructure. This is clearly seen in the microstructure shown in Figure 6 (a). Furthermore, it was verified that the reduction grain size profile has a particular feature (an exponential decay), as presented in Figure 7.

The best magnetic properties and microstructural homogeneity were obtained for the alloy decrepitated and subsequently milled for 4.5 ks (75 min). The remanence reached 1020 mT, although this value is somewhat below to that (1200 mT) reported for a $Pr_{16}Fe_{76}B_8$ magnet prepared using the "roller" ball mill [(4)]. On the other hand, $\mu_{0i}H_c$ reached 1420 mT, 10 % superior than the value reported for magnets produced using RBM [(4)]. The microstructure of this sintered magnet is presented in Figure 6 (b).

The last condition studied concerns magnets obtained from the decrepitated alloy milled for 5.4 ks (90 min). As can be seen in Figure 5, there was a reduction in B_r after 4.5 ks, probably due to the reduction of the alignment degree of the $Pr_2Fe_{14}B$ phase, which is being confirmed using X-ray pole figure analyses. The microstructure of the magnet processed at 5.4 ks is shown in Figure 6 (c). There is a similarity of the grain structure of this sample compared to the previous case (magnet processed at 4.5 ks), so that no significant change in the intrinsic coercivity would be expected, as verified in Figure 5.

It is worthwhile noting that increasing the milling speed, with constant milling time, the density of the magnets also increases, probably due to a better sinterability. The tendency of the density increasing with the rotational milling speed was also noted (probably due to the reduction of the particle size after milling). A summary of the HD sintered $Pr_{16}Fe_{76}B_8$ magnetic properties and the results of microstructural parameters and densities are presented in Table 1 and 2, respectively.

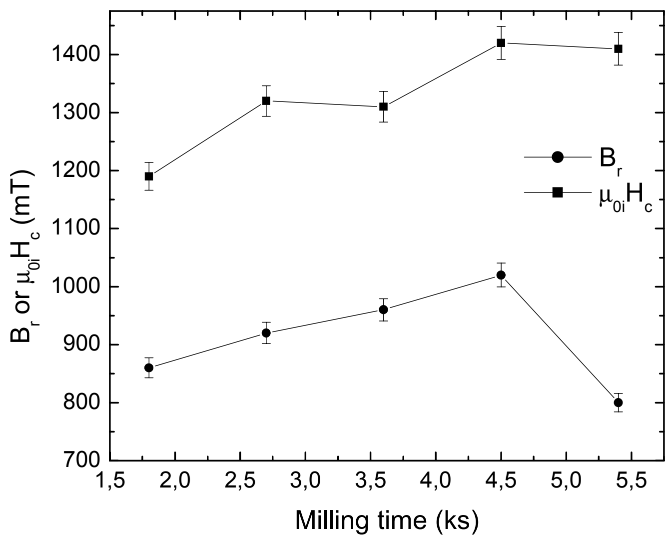
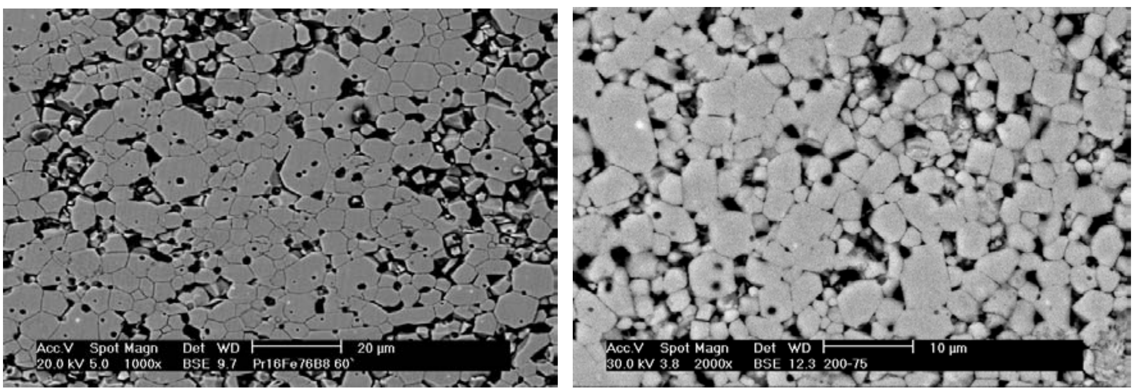
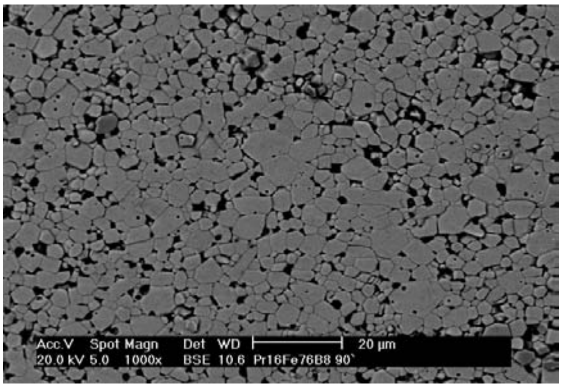


Figure 5 – Variation of remanence and intrinsic coercivity with milling time from $Pr_{16}Fe_{76}B_8$ alloy milled at 200 rpm.



(a) (b)



(c)

Figure 6 – General view of the microstructure of $Pr_{16}Fe_{76}B_8$ magnet produced from the decrepitated ingot milled at 200 rpm for (a) 3.6 (b) 4.5 and (c) 5.4 ks.

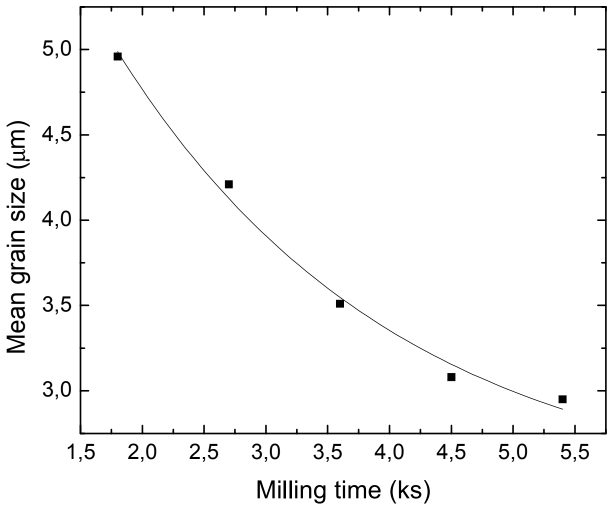


Figure 7 – Exponential profile of the grain size reduction for the $Pr_{16}Fe_{76}B_8$ magnets produced from the decrepitated ingot milled at 200 rpm.

Table 1 – Magnetic properties for the $Pr_{16}Fe_{76}B_8$ HD sintered magnets.

Speed (rpm)	**Milling time (kiloseconds)**	**B_r (mT) (± 2%)**	**$\mu_{0i}H_c$ (mT) (± 2%)**	**$(BH)_{max}$ (kJm^{-3}) (± 2%)**	**SF (no unit)**
150	1.8	570	920	55	0.35
	2.7	610	1070	56	0.20
200	1.8	860	1190	134	0.54
	2.7	920	1320	162	0.65
	3.6	960	1310	176	0.79
	4.5	1020	1420	200	0.79
	5.4	800	1410	118	0.70
250	1.8	660	1100	77	0.36
	2.7	820	1430	121	0.49
300	1.8	740	1370	96	0.51
	2.7	780	1400	109	0.46

Table 2 – Microstructural parameters and densities for the $Pr_{16}Fe_{76}B_8$ HD sintered magnets.

Speed (rpm)	**Milling time (kiloseconds)**	**Grain size (μm)**	**Standard deviation (μm)**	**Density (gcm^{-3}) (± 0.5%)**
150	1.8	7.67	4.59	7.10
	2.7	6.68	2.84	7.10
200	1.8	4.96	2.78	7.34
	2.7	4.21	2.80	7.35
	3.6	3.51	2.00	7.42
	4.5	3.08	1.60	7.48
	5.4	2.95	1.68	7.43
250	1.8	4.61	2.50	7.37
	2.7	3.33	1.59	7.47
300	1.8	3.58	1.80	7.46
	2.7	3.00	2.05	7.47

CONCLUSIONS

The present studies show clearly that, employing the appropriate parameters for high-energy milling, it is possible to produce good permanent sintered magnets. Satisfactory overall magnetic properties were obtained for the magnet prepared with the alloy hydrogen decrepitated and milled at 200 rpm for 4.5 ks (75 min). High-energy milling had the effect of improving the intrinsic coercivity of the PrFeB HD sintered magnet, but at the expenses of the remanence and energy product. The processing time of the magnets was dramatic reduced (around 90%) compared with the conventional “roller” ball milling.

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