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Comparison of the Kerr effect and X-ray pole figure methods for determining crystallographic texture in PrFeB magnets

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Abstract

In this study, magnetic domains in $Pr_{16}Fe_{76}B_8$ sintered magnets have been observed by Kerr effect and a histogram of the angular distribution of domain orientations has been used to determine the magnetic texture ($\langle \cos \Phi \rangle$). The degree of easy-axis alignment of $Pr_2Fe_{14}B$ matrix grains in these magnets has been also determined by X-ray pole figure analysis using the (0 0 4) reflection. The (0 0 4) pole figure measurements were carried out by the Schultz's reflection method. The (0 0 4) normalized intensity data has been fitted for a Gaussian distribution and the degree of crystal alignment, $\langle \cos \Theta \rangle$, has been calculated using the Stoner–Wohlfarth model. Comparison of these methods has been carried out. It has been shown that in magnets with medium and high degrees of crystallographic alignment, the pole figure values are higher than that obtained by the Kerr effect method. Conversely, in magnets with low degrees of alignment, $\langle \cos \Theta \rangle$ is lower than $\langle \cos \Phi \rangle$.

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Keywords: Magnets; Texture; PrFeB alloys

1. Introduction

X-ray diffraction and Kerr effect have been used extensively to determine the degree of texture in permanent magnets (see, for example, Refs. [1–14]). Even though the two methods have been used successfully in the past, comparison between them has not yet been carried out. In this investigation, the degree of crystallographic alignment of various $Pr_{16}Fe_{76}B_8$ sintered magnets has been determined using Kerr effect and X-ray pole figure analysis. The degree of easy-axis alignment data, obtained by these methods has been assessed. Sintered magnets with high, medium and low degrees of crystal alignment, and prepared using the hydrogen decrepitation (HD) process, have been studied. In this study, the ratio of remanence to saturation magnetization (B_r/M_s) has been used as reference to compare the results of X-ray diffraction and Kerr effect.

2. Experimental

A commercial $Pr_{16}Fe_{76}B_8$ (wt%: 34.24Pr-64.45Fe-1.31B) alloy in the as-cast state was used

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in this study. To produce the sintered Pr-based magnets using the HD process [15,16], 35 g of the bulk ingot was placed in a stainless steel hydrogenation vessel and was then evacuated to backing-pump pressure. Hydrogen was introduced to a pressure of 1 bar, which resulted in decrepitation of the bulk material. The standard decrepitated hydride material was then transferred to a "roller" ball-mill under a protective atmosphere and milled for several hours using cyclohexane as the milling medium. The resultant fine powder was then dried for 1 h and transferred to a small cylindrical rubber tube under a nitrogen atmosphere. The fine powder was aligned by pulsing three times in a 6 T magnetic field, pressed isostatically at 1000 kg cm^{-2}, vacuum sintered for 1 h at 1060°C and cooled in the furnace ($\sim$3.5°C min^{-1}). Heat treatment was carried out under vacuum at 1000°C for 24 h. Magnetic measurements of the HD sintered magnets were performed in a permeameter after saturation in a pulsed field of 6 T.

The milling stage and heat treatment were used to change the degree of grain alignment in the $Pr_{16}Fe_{76}B_8$ magnets as reported previously [16]. Sintered magnets prepared from powders milled for a short time (9 h) were considered to possess low degrees of crystal alignment. Medium degrees of crystal alignment were attributed to magnets prepared from powders milled for moderate times (27 h). High degrees of alignment were assumed in sintered magnets produced from powders milled for prolonged times (45 h). The samples, as-sintered and heat treated, were examined using a Rigaku diffratometer (DMAX-2000) at various cross sectional regions of the sintered magnet (longitudinal for Kerr effect). Previous studies [5,12] used the (0 0 6) pole figure to determine the texture in Nd-based magnets. In this study, preliminary evaluation showed that the (0 0 6) reflection is close to the (3 3 1), (4 0 2) and (3 1 4) reflections, all with strong relative intensities, which could cause overlap in the X-ray pole figure measurements. Therefore, the (0 0 4) reflection was chosen in this investigation. Measurements of (0 0 4) pole figures were carried out by the Schulz's reflection method with a diffractometer, using the CrKα radiation and Kβ filter [1]. The tilt angle (α) was varied from 0° to 75° in steps of 5°. The angle of rotation, azimuth angle (β), was varied from 0° to 360° in steps of 5° (5 s per step). The intensities of the pole figure data were normalized by

$$I(\alpha_j) = \frac{\sum_{i=1}^{72} f(\alpha_j, \beta_i)}{72.I(\alpha_1)}, \quad j = 1, 16. \tag{1}$$

The (0 0 4) normalized intensity data was then fitted for a Gaussian distribution, and $\langle \cos \Theta \rangle$ was calculated based on the Stoner–Wohlfarth model [17], using:

$$\langle \cos \Theta \rangle = \frac{B_r}{M_s} = \frac{\int_{.0}^{.\pi/2} \exp(-\alpha^2/2\sigma^2)\sin\alpha\cos\alpha\, d\alpha}{\int_{.0}^{.\pi/2} \exp(-\alpha^2/2\sigma)\sin\alpha\, d\alpha}, \tag{2}$$

where M_s is the saturation magnetization of the magnet, B_r is the remanence of the magnets, σ is the full-width at half-maximum intensity (FWHW) of the Gaussian function and α is the angle between the tetragonal c-axis and the applied field [11]. Data collection were carried out using a Rigaku computer program with background subtraction.

The saturation magnetization for the $Pr_{16}Fe_{76}B_8$ magnets was estimated (assuming that all Fe in the magnet exists in the $Pr_2Fe_{14}B$ phase) using the following expression [11]:

$$M_s = M_s^N \frac{W_{Fe} W_N^M \rho_S}{100\ 14\ W_{Fe}^M \rho_N}, \tag{3}$$

where M_S^N is the saturation magnetization of $Pr_2Fe_{14}B$ at 300 K (1.56 T [17]), W_{Fe} is the weight percentage of Fe in the magnet (64.45%), W_{Fe}^M is the molecular weight of Fe (55.85 g/mol), W_N^M is the molecular weight of $Pr_2Fe_{14}B$ (1074.47 g/mol [18]), ρ_N is the X-ray density of $Pr_2Fe_{14}B$ (7.53 g/cm^3 [19]) and ρ_S is the measured specific density of the sintered magnet. The densities of the permanent magnets were measured using a liquid displacement system.

Microstructures were examined with an optical microscope coupled to an image analyzer to observe the magnetic domains. A histogram of the angular distribution of the "c" directions of the grains (determined from magnetic domain orientations) and alignment direction was prepared [14].

To measure the angle between the individual grain orientation (Φ) and the alignment direction, five different fields were considered in each sample. In each field, more than 450 angles were measured.

3. Results and discussion

Fig. 1 shows the (0 0 4) pole figures for $Pr_{16}Fe_{76}B_8$ sintered magnets with low and medium degrees of crystallographic alignment. The circular lines, which correspond to changes in the intensity of the (0 0 4) diffraction lines, are more concentrated in the center for the magnet with better alignment. Fig. 2 shows the (0 0 4) pole figures and a three-dimensional (3-D) plot for a permanet magnet with high degree of crystal alignment. The circular lines, in this case, are concentrated in the center of the axis with a very sharp and well-defined 3-D pattern. Thus, short and long milling times produced magnets with low ($\langle \cos\Theta \rangle = 0.63$) and high ($\langle \cos\Theta \rangle = 0.96$) degrees of crystal alignment. Moderate milling times, as expected, produced sintered magnets with medium degrees

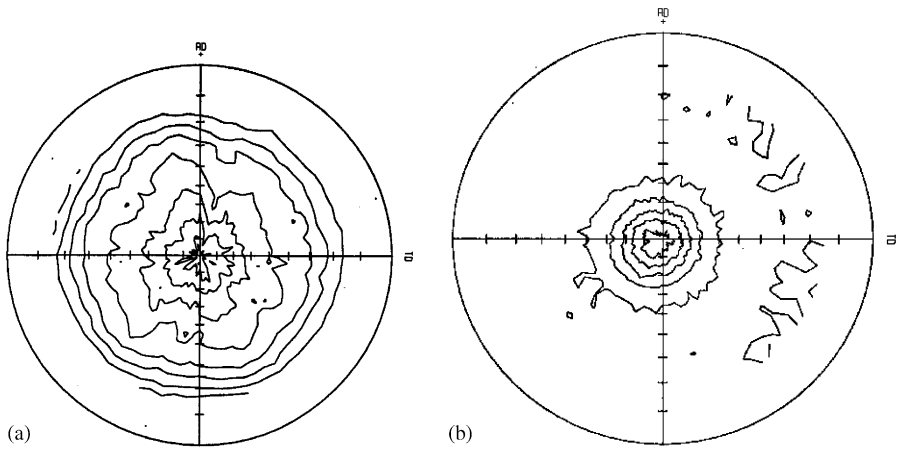

Fig. 1. (0 0 4) pole figures for magnets with (a) low and (b) medium degree of crystal alignment ($\langle \cos\Theta \rangle = 0.63$ and 0.89, respectively). Intensity of isolines in times random (TR): (a) 0.2, 0.4, 0.7, 1.1, 1.3, 1.6 and 1.8; (b) 0.9, 1.7, 2.6, 3.4 and 4.3.

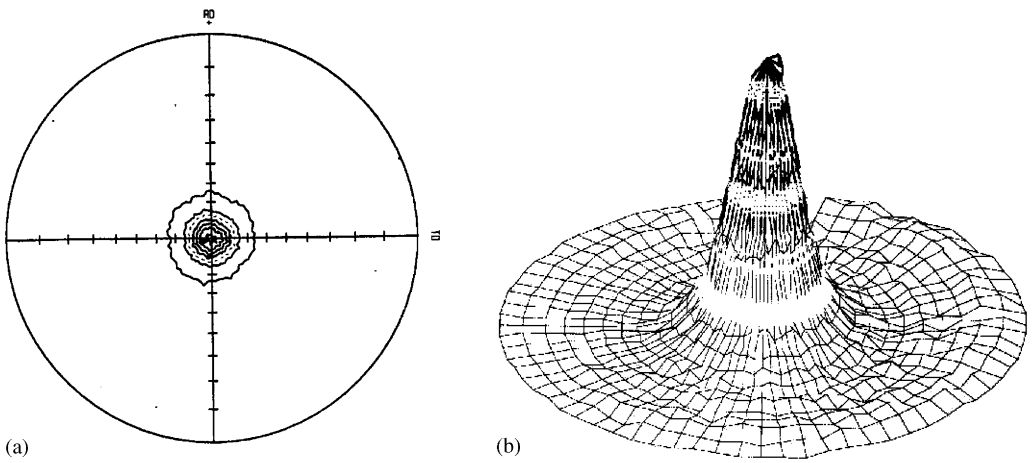

Fig. 2. (0 0 4) pole figure (a) and 3-D plot (b) for a magnet with high degree of alignment ($\langle \cos\Theta \rangle = 0.96$). Isolines intensity (TR): 1.9, 3.8, 5.8, 7.7, 9.6, 11.5, 13.4 and 15.4.

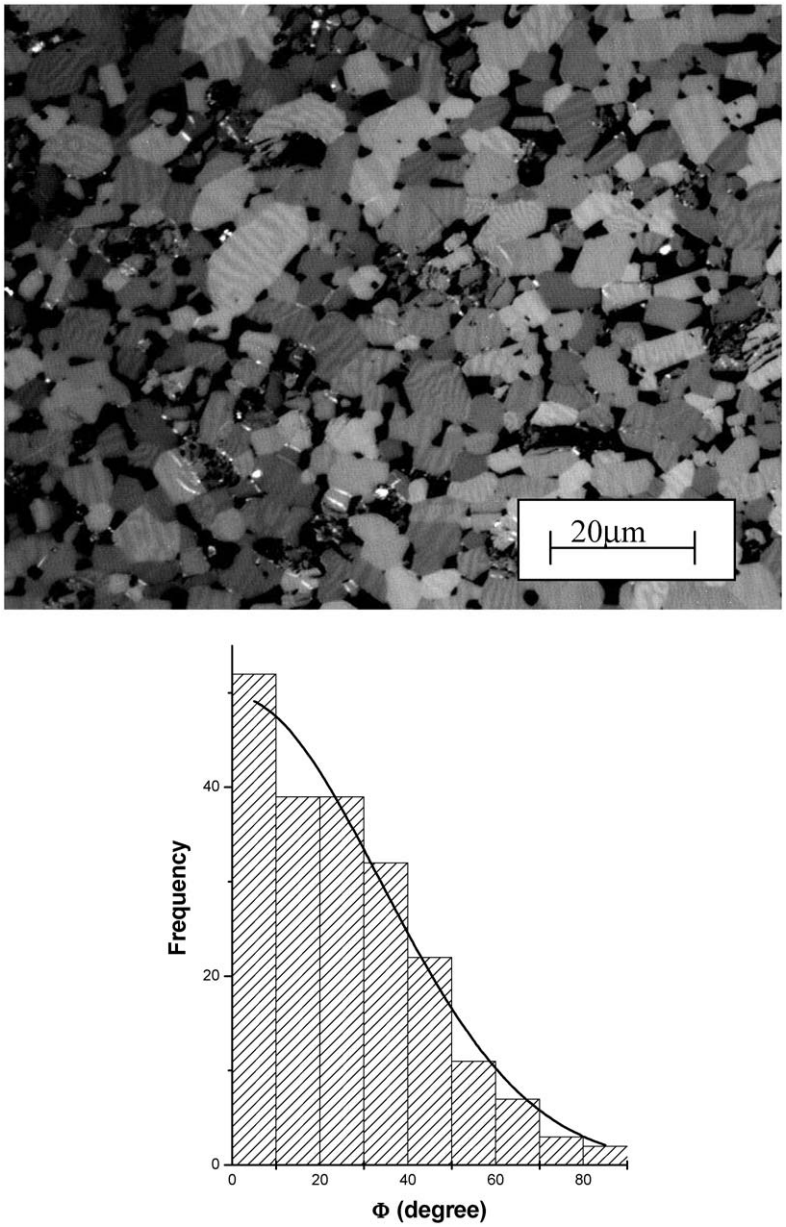

Fig. 3. Magnetic domains and histogram obtained by Kerr technique for a magnet with low degree of alignment ($\langle \cos \Phi \rangle = 0.77$).

of crystallographic alignment ($\langle \cos \Theta \rangle = 0.89$). It has been possible to establish a direct correlation between milling time and texture from the X-ray pole figure measurements. Based on these results, magnets with $\langle \cos \Theta \rangle$ less than 0.80 and more than 0.90 were considered to be with low and high degrees of crystallographic alignment.

Fig. 3 shows the magnetic domains obtained by Kerr effect and the corresponding histogram of the angular distribution of easy axes grain direction

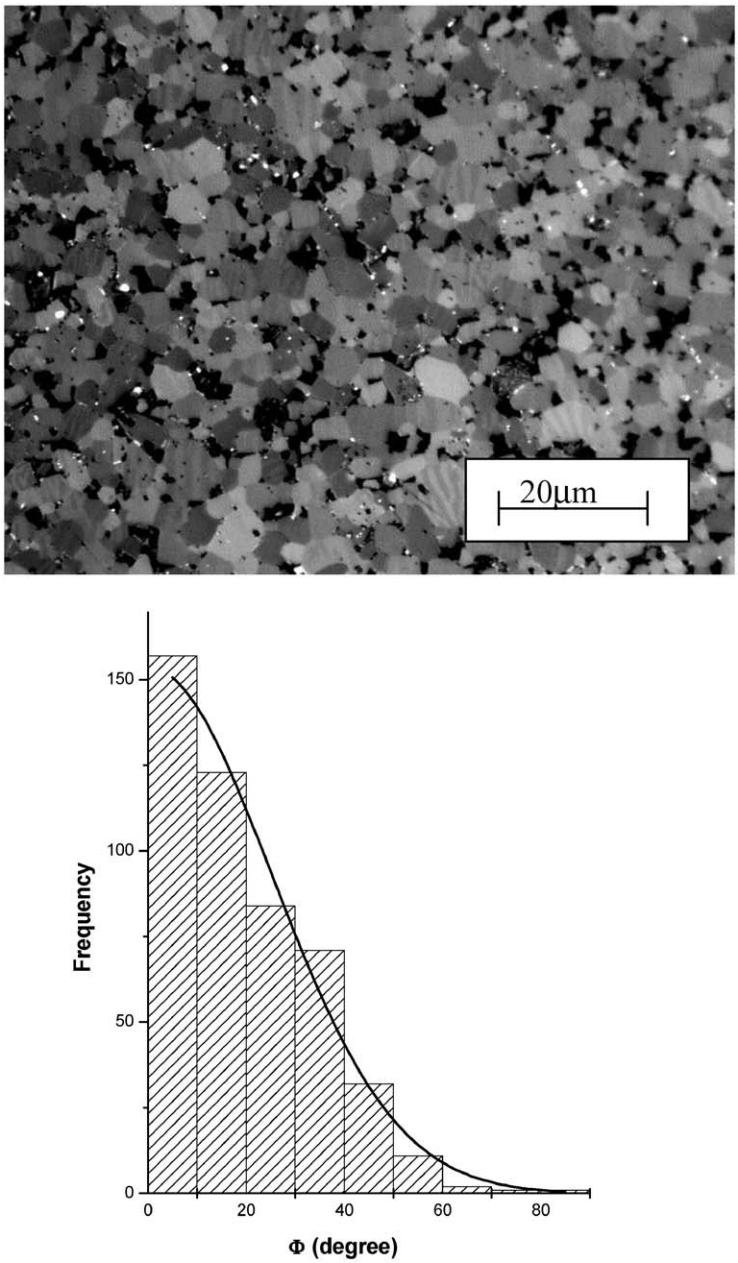

Fig. 4. Magnetic domains and histogram obtained by Kerr technique for a magnet with medium degree of alignment ($\langle \cos \Phi \rangle = 0.83$).

for the magnet produced from powders milled for a short time. The degree of crystal alignment ($\langle \cos \Phi \rangle = 0.77$) determined by this method was slightly higher than that determined from the X-ray pole figure ($\langle \cos \Theta \rangle = 0.63$). This value still represents a magnet with low or poor degree of crystallographic alignment. Fig. 4 shows the magnetic domains and histogram of the magnet prepared from powders milled for a moderate time. Conversely, in this case, the degree of crystal

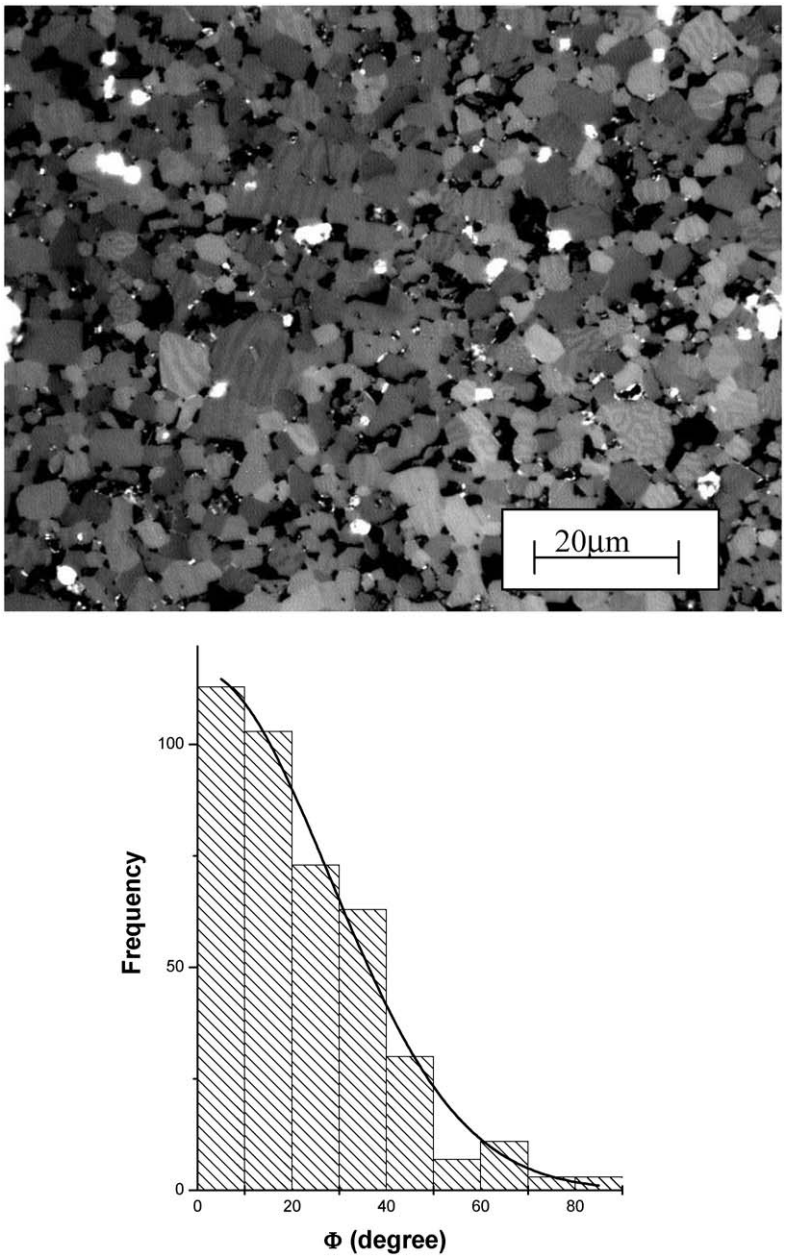

Fig. 5. Magnetic domains and histogram obtained by Kerr tecchnique for a magnet with high degree of alignment ($\langle \cos \Phi \rangle = 0.80$).

alignment ($\langle \cos \Phi \rangle = 0.83$) determined by Kerr technique was slightly less than that determined from the X-ray pole figure ($\langle \cos \Theta \rangle = 0.89$). Nevertheless, this magnet can be considered to have a medium degree of crystallographic alignment (from 0.80 to 0.90). Fig. 5 shows the magnetic domains and histogram for the magnet prepared using powders milled for a prolonged time. Quite surprisingly at first glance, the degree of crystal alignment ($\langle \cos \Phi \rangle = 0.80$) determined by the Kerr technique is less than that determined from the X-ray pole figure ($\langle \cos \Theta \rangle = 0.96$). In

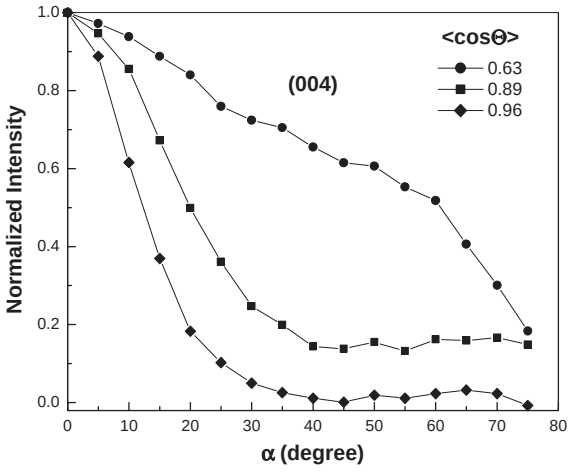

Fig. 6. Normalized X-ray intensities as a function of angle α for three magnets with distinct degrees of alignment, for the reflections (0 0 4).

the present classification, based on the X-ray results, this value is far from being included as high degree of alignment. This behavior can be easily understood by realizing that it becomes very difficult to determine the crystallographic alignment using the Kerr technique in magnets with very fine grain sizes. It has been reported [10] that practical crystallographic alignment estimates can be made only for large-grained materials, with grain sizes of the order of microns. This technique can, in principle, provide an accurate estimate of granular alignment but is sensitive only to the exposed surface [10] and care needs to be taken while probing various regions of the sintered magnet.

Fig. 6 shows the X-ray pole figure normalized intensities as a function of angle α for three magnets, with low, medium and high degrees of crystallographic alignment. A clear distinction between magnets with medium and high degrees of crystal alignment can be seen. A comparison with histograms shown in Figs. 4 and 5 reveals the improved resolution of X-ray diffraction pole figures for magnets with high degrees of crystallographic alignment. The resolution of the X-ray technique diminishes for magnets with degree of crystal alignment higher than 0.96. The $\langle \cos \Theta \rangle$ obtained by pole figure analysis was found to be less sensitive at high degrees of alignment because of the $I(\alpha)$ broadening [21]. The instrumental profile is very broad in the Schulz's method. Besides, defocusing effects and other geometrical imperfections also occur. For low degrees of alignment, the $I(\alpha)$ is influenced by the neighboring diffraction peaks. The size of the magnet's cystallites also causes $I(\alpha)$ broadening [21]. It has been reported [10] that the main drawback with X-ray diffraction techniques in the determination of crystallographic alignment is that they probe only the first few microns of the specimen's exposed surface, and therefore, do not measure the bulk properties. In this investigation care has been taken to examine various regions of the sintered magnets to avoid such problems, and coherent results have been obtained. Bearing in mind that hot pressed magnets are more likely to have larger grains than sintered magnets [20], difficulties related to probing could be a problem in this kind of magnet. Extremely large grains do not align properly and are non-representative of the bulk crystallographic alignment in magnets. The fine milled powder used for the production of sintered magnets is sieved prior to the magnetic alignment and pressing stages, to avoid coarse particles in the green body and consequent large grains in the sintered magnet.

Table 1 gives a summary of degree of crystal alignment, magnetic properties and density of all the magnets that have been studied here. The remanence of a permanent magnet depends directly on the degree of crystallographic alignment, volume fraction and saturation polarization of the matrix phase, as well as on the magnet density. Thus, the remanence to saturation magnetization ratio should only be used to compare the degree of alignment in $Pr_{16}Fe_{76}B_8$ sintered magnets, if the volume fraction of the matrix phase and density are constant in all the sintered magnets that are being compared. Even though this is not the case in magnets studied here, the values of B_r/M_s also confirm the general tendency of degree of crystallographic alignment measured by domains and pole figures. The B_r/M_s value is not valid for magnets prepared using prolonged milling times because the volume fraction of the matrix phase is reduced by oxidation of the very fine powder [21]. In this case the ratio B_r to M_s

Table 1
Degree of alignment determined by domains and X-ray, magnetic properties and density of the HD sintered $Pr_{16}Fe_{76}B_8$ magnets

Milling time	Magnet condition	$\langle \cos \Phi \rangle$	B_r/M_s	$\langle \cos \Theta \rangle$	B_r(T)	$\mu_o iHc$(T)	ρ_s(g/cm^3)
Short	As-sintered	0.77±0.01	0.75±0.01	0.63±0.01	1.01±0.02	1.36±0.03	7.30±0.02
Medium	As-sintered	0.83±0.01	0.81±0.02	0.89±0.01	1.10±0.02	1.32±0.03	7.38±0.02
	Heat-treated	0.82±0.01	0.83±0.02	0.92±0.01	1.12±0.02	1.67±0.03	7.39±0.02
Long	As-sintered	0.80±0.01	0.85±0.02	0.96±0.01	1.14±0.02	1.39±0.03	7.32±0.02
	Heat-treated	0.78±0.01	0.86±0.02	0.97±0.01	1.15±0.02	1.49±0.03	7.30±0.02

measures also the variation in volume fraction of the permanent magnet.

4. Conclusions

The X-ray pole figure method has been found to be a rapid and reliable method for determining low, medium and high degrees of crystallographic alignment in sintered Pr-based magnets. The Kerr effect technique, on the other hand, proved to be time-consuming and inappropriate for permanent magnets with high degrees of crystallographic alignment. This is attributable to the fine grain size of these magnets. However, the Kerr technique can provide a reasonable estimate for magnets with low and medium degrees of crystal alignment. Use of the ratio B_r to M_s, to compare crystal alignment between magnets is appropriate only if the magnets have been processed under similar conditions, i.e., the volume fraction of the matrix phase and density are constant in all magnets. In this case, accuracy is compromised because B_r also depends on these parameters.

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