MAGNETIC PROPERTIES OF Pr-Fe-B SINTERED MAGNETS PRODUCED FROM HYDRIDE POWDER AND FROM PARTIALLY AND TOTALLY DESORBED HYDRIDE POWDER

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ABSTRACT

The effect of a post-sintering heat treatment on the magnetic properties of Pr-Fe-B based magnets has been studied. For particular processing conditions, annealing the $Pr_{16}Fe_{76}B_8$ magnets at 1000 °C resulted in an increase in iHc from 14.9 to around 17.5 kOe. The magnetic properties, before and after annealing, of magnets prepared from this standard HD powder were compared with those of samples prepared from partially and totally desorbed HD powder. Sintered magnets prepared from the hydrided powder exhibit a superior intrinsic coercivity compared to that of magnets prepared from the totally desorbed powder. However, the remanence and energy product of the latter are significantly higher. The squareness factor (0.93) has been improved considerably and good overall magnetic properties (Br~11.7 kG, $(BH)_{max}$~35.2 MGOe and iHc~15.2 kOe) have been achieved for the sintered magnet prepared from partially desorbed powder.

1. Introduction

Previous studies have shown that the magnetic properties of Nd/Pr-Fe-B-(Cu) type permanent magnets can be influenced substantially by the initial state of the alloy[1,2,3,4]. It has been shown[5] for HD magnets based on the alloys $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ and $Pr_{16.9}Fe_{79.1}B_4$ that the milling time and a high temperature heat treatment can affect significantly the final magnetic properties of the sintered magnets. In the present work a similar investigation using the HD process has been carried out for magnets based on the alloy $Pr_{16}Fe_{76}B_8$. The corresponding Nd-based sintered HD magnets have also been prepared for a comparison.

It has been reported[6] that in $Pr_2Fe_{14}B$, when in the fully saturated hydrided condition, the easy direction of magnetization changes from the tetragonal c-axis to easy basal plane. This, in practice, could produce radially anisotropic magnets[7] or, at least, affect to some degree the remanence and squareness factor of Pr-Fe-B magnets prepared using the hydrogen decrepitation process. It has also been shown[8] that Pr-Fe-B-Cu magnets produced by the HD process exhibit uniaxial anisotropy, although with lower remanence values than those of the hot-pressed Pr-Fe-B-Cu magnets[9] based on a similar composition. If the anisotropy factor is drastically reduced by hydrogen then this would influence the degree of c-axis alignment in the green compact and hence the squareness of the final loop.

Recently, the influence of partial and complete desorption of the hydrided powder prior to magnetic processing on the degree of alignment of HD sintered magnets of a $Pr_{16}Fe_{76}B_8$ alloy has been investigated[4]. The crystal alignment of these sintered magnets have been investigated by X-ray diffraction. In the present work, the magnetic properties, before and after annealing, of magnets prepared from partially and totally desorbed HD powder of a $Pr_{16}Fe_{76}B_8$ alloy were compared with those of samples prepared from the standard HD powder.

2. Experimental

Alloy ingots investigated in this work were prepared by induction melting the pure constituents under a purified argon atmosphere (composition is given in Table I). In order to produce the magnets via the HD process[10], small pieces of the bulk ingot were placed in a stainless steel hydrogenation vessel which was then evacuated to backing-pump pressure and hydrogen was then introduced to a pressure of 10 bar. This resulted in decrepitation of the bulk material and the decrepitated material was evacuated to backing-pump pressure for 1 hour and then transferred to a "roller" ball-mill under a protective nitrogen atmosphere and milled using cyclohexane as the milling medium.

The resultant fine powder was then dried and transferred under dry nitrogen to a small cylindrical rubber tube, pulsed in a magnetic field of 60 kOe and isostatically pressed. The green compacts were vacuum sintered at 1060°C for 1 hour followed by a furnace cooling (~3.5°C/min) and the magnetic properties determined in a permeameter. The as-sintered magnets then received a heat treatment[8,9] under vacuum at 1000 °C for 24 hours and the magnetic properties were re-measured.

Table I. Composition of the as-cast alloys (RE = Pr , Nd).

Atomic %	Wt %		
	RE	Fe	B
$RE_{16}Fe_{76}B_8$	35.0	63.7	1.30

Partially desorbed (PD) powder was prepared from the decrepitated hydride by a heat treatment in vacuum at 300°C for 5 hours. Total desorption of the material was also carried out in vacuum but at 600°C for 5 hours. The partially and totally desorbed (TD) material was then processed in the same manner as the decrepitated hydride material according to the scheme illustrated in fig. 1.

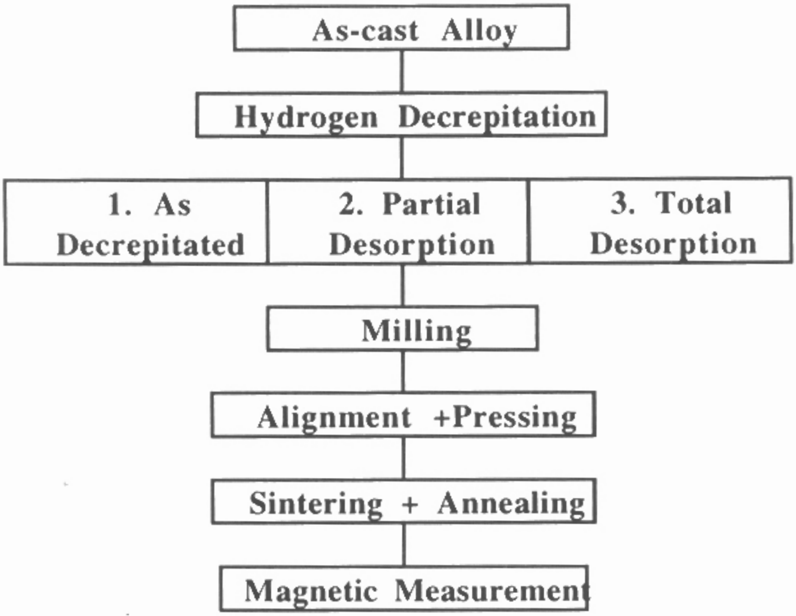

Fig. 1. HD sintered magnets processing routes. Using : (1) Standard Hydrogen decrepitation, (2) Partially desorbed and (3) Totally desorbed material.

3. Results and Discussion

The effects of milling time and annealing at 1000°C for 24 hours are shown in Fig.2. The $Pr_{16}Fe_{76}B_8$ magnet prepared from the standard HD material exhibits a substantial increase in iHc in the powder milled for 18 and 27 hours. There is a maximum intrinsic coercivity of around 17.5 kOe on annealing the HD alloy milled for 18 hours and the demagnetization curves for this $Pr_{16}Fe_{76}B_8$ HD magnet, before and after annealing, are shown in fig.3 .

The remanence and energy product are improved as the alloy is milled for longer times with no large changes on annealing. A very square demagnetization loop (squareness factor: SF=0.93) is obtained when the milling time reaches 45 hours, as shown in fig. 4. The intrinsic coercivity obtained in the present magnets is lower than that of $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD sintered magnets (~20 kOe)[4,8], however the present $Pr_{16}Fe_{76}B_8$ HD magnets exhibit higher Br, $(BH)_{max}$ and squareness factor.

$Nd_{16}Fe_{76}B_8$ sintered magnets prepared from the standard HD material, milled for 18 hours, showed an inferior squareness factor (SF=0.75) and intrinsic coercivity (iHc= 12.6 kOe) than the $Pr_{16}Fe_{76}B_8$ magnets. The remanence and energy product however, were higher in the Nd-based magnets (Br=12.5 kG and BH_{max}=37.4 MGOe). These magnetic properties are for the Nd-based magnets in the as-sintered condition since, for these magnets, the annealing at 1000°C for 24 hours was found to be detrimental to the magnetic properties (see Fig. 5).

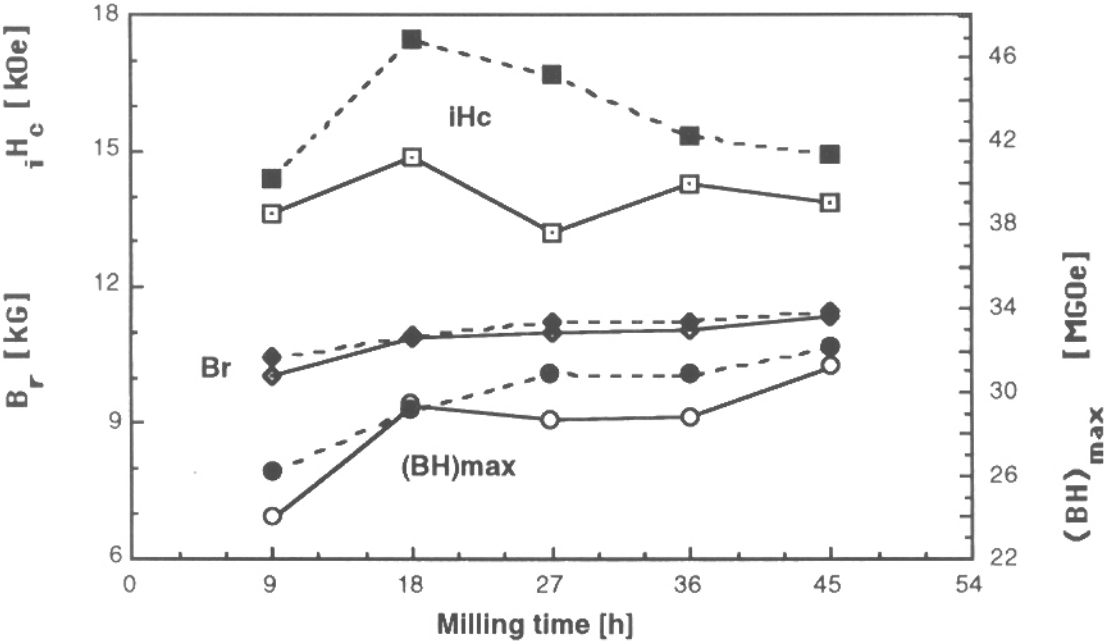

Fig. 2. Variation of (BH)max (o,●), iHc (⊡, ■) and Br (◊,◆) with the milling time for sintered and slow cooled magnets of $Pr_{16}Fe_{76}B_8$ alloy (Open symbols: as-sintered values; full symbols : annealed 1000°C, 24 hours, slow cooled).

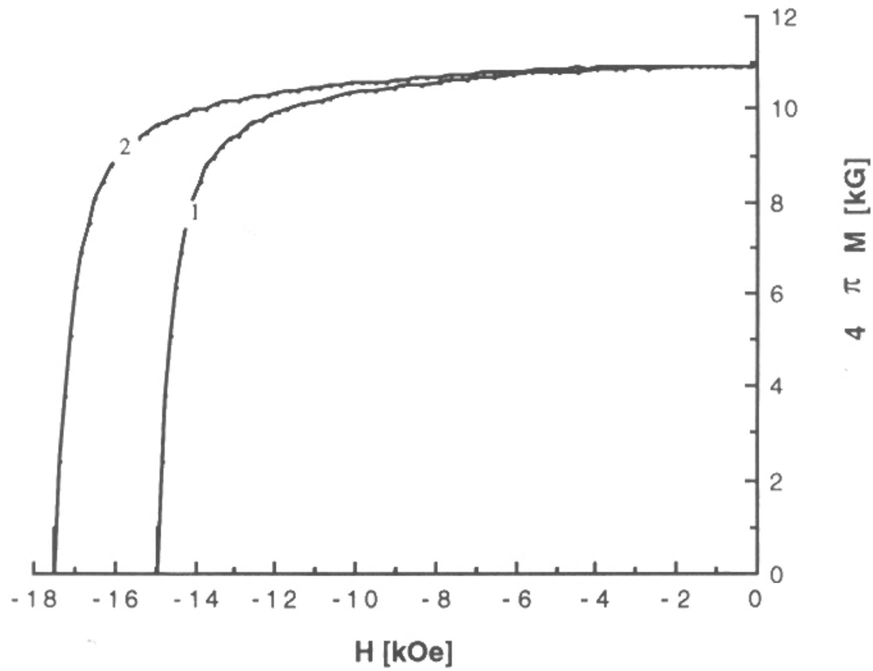

Fig. 3. Demagnetization curves for sintered (1) annealed (2) $Pr_{16}Fe_{76}B_8$ magnets prepared using the HD powder milled for 18 hours.

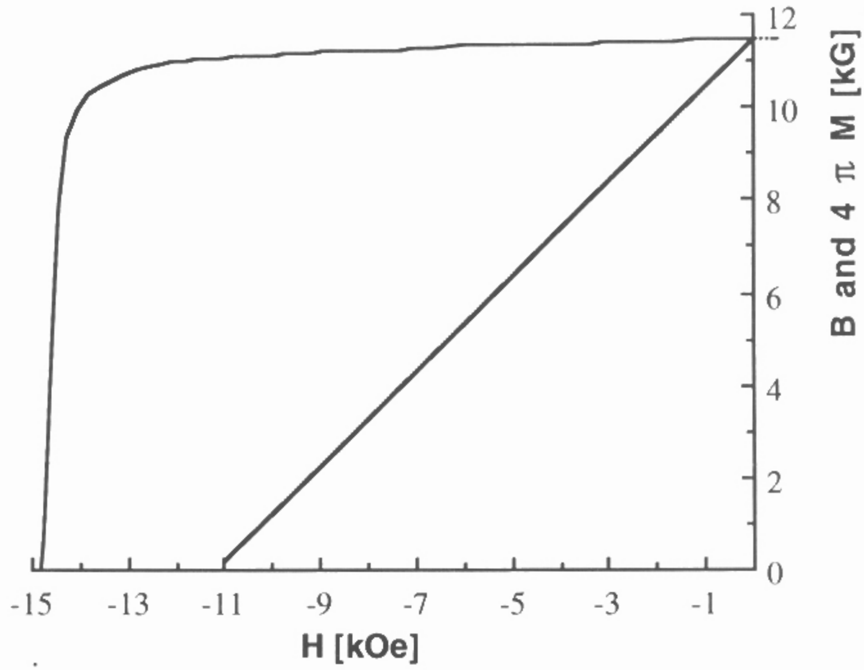

Fig. 4. Demagnetization curves for annealed (1000°C, 24 hours, slow cooled) $Pr_{16}Fe_{76}B_8$ magnets prepared using the HD powder milled for 45 hours.

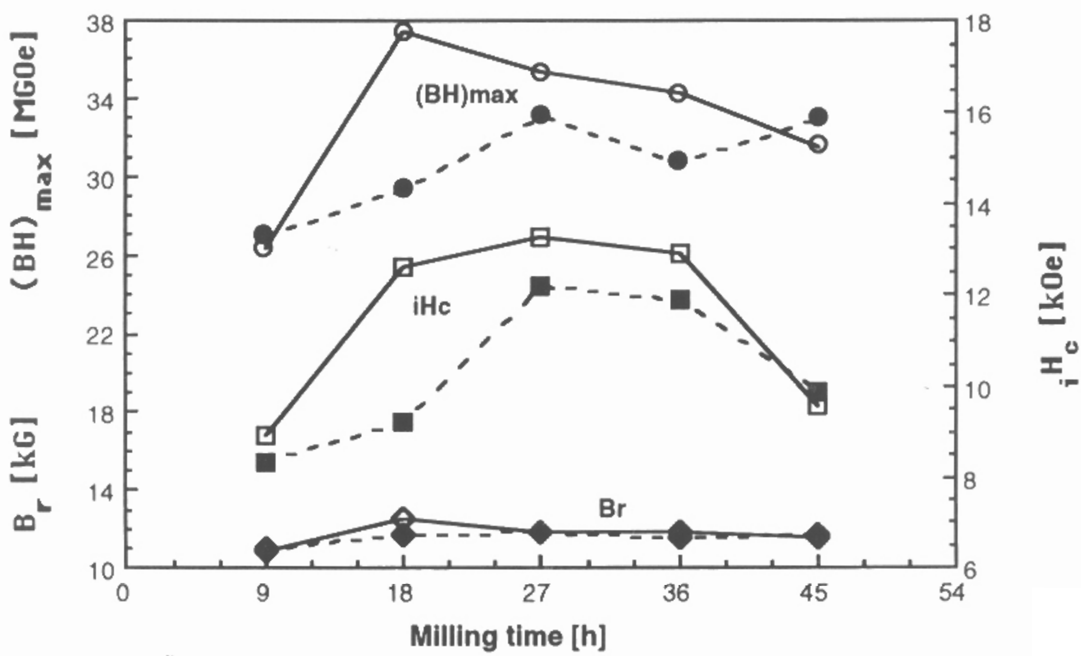

Fig. 5. Variation of (BH)max (o,●), iHc (▣, ■) and Br (◊,◆) with the milling time for sintered and slow cooled magnets of $Nd_{16}Fe_{76}B_8$ alloy (Open symbols: as-sintered values; full symbols: annealed 1000°C, 24 hours, slow cooled).

Previous study[4] on the desorption behaviour of hydrogen from the $Pr_{16}Fe_{76}B_8$ alloy, investigated by mass spectroscopy, showed two desorption peaks, one at 145 °C and the other at 580 °C. The partial desorption of hydrogen from the decrepitated material was therefore carried out at 300°C as this is the upper limit of the low temperature desorption peak. For the full desorption of hydrogen, a temperature of 600°C was employed, which is close to the upper limit of the high temperature peak. A higher temperature was not employed to avoid agglomeration of the powder particles. In both cases the lowest possible desorption temperature was chosen in order to minimize any oxidation of the powder.

The effect of complete desorption of the HD powder prior to magnetic processing was to increase the remanence and decrease the intrinsic coercivity of the sintered magnets compared with the corresponding properties of the standard HD magnet subjected to the same milling and heat treatments. The demagnetization curves for the as-sintered and annealed magnets prepared from a totally desorbed HD powder are shown in fig. 6.

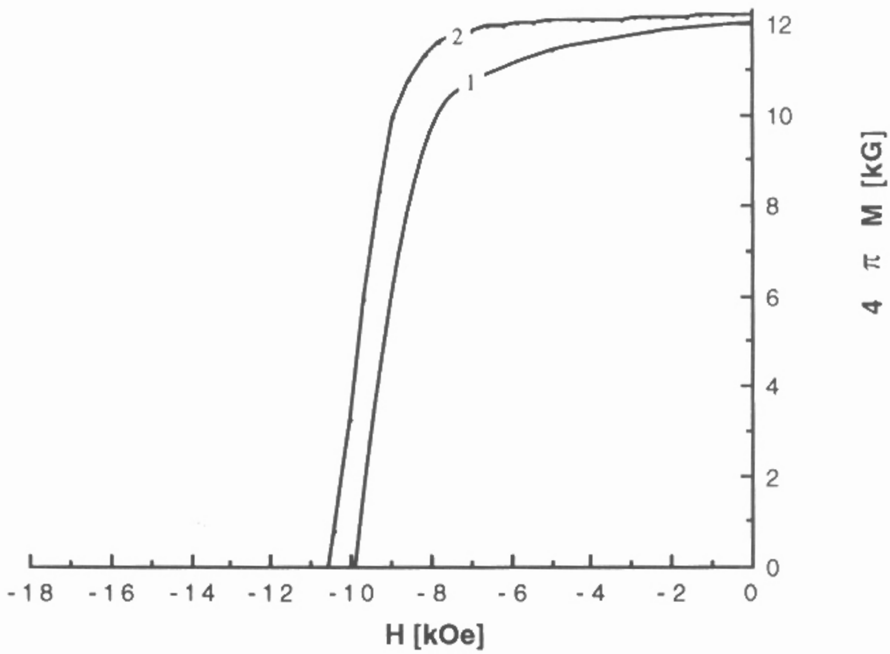

Fig. 6. Demagnetization curves for sintered (1) annealed (2) $Pr_{16}Fe_{76}B_8$ magnets prepared using the TD powder milled for 18 hours.

The effect of partial desorption of the HD alloy prior to magnetic processing was also to increase the remanence and to decrease the intrinsic coercivity but both to a lesser extent than in the previous case. The demagnetization curves for the as-sintered and annealed magnets prepared with a partially desorbed HD alloy are shown in fig. 7. A very square loop is obtained for the annealed magnet and the best overall magnetic properties are achieved in this case.

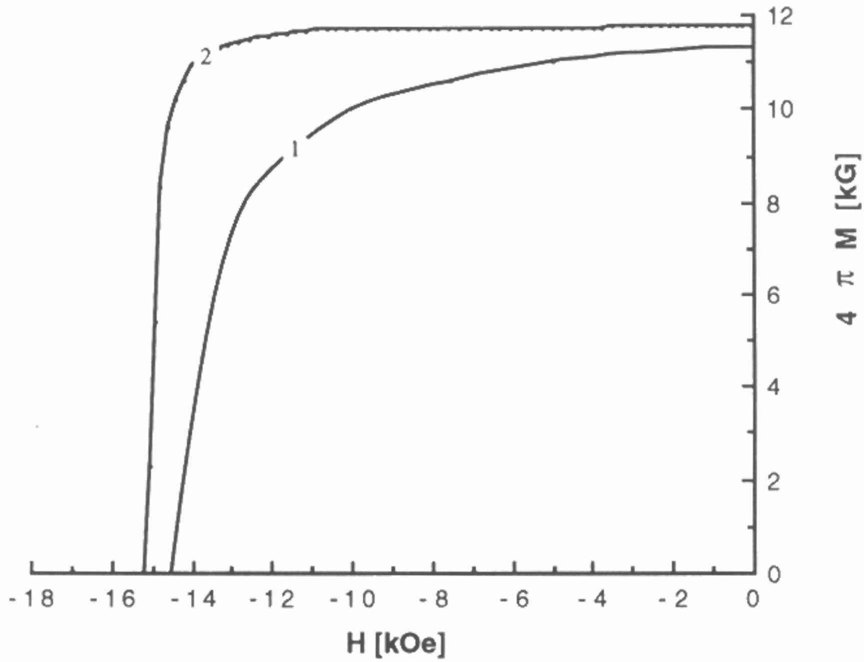

Fig. 7. Demagnetization curves for sintered (1) annealed (2) $Pr_{16}Fe_{76}B_8$ magnets prepared using the PD powder milled for 18 hours.

The magnetic behaviour of the HD, PD and TD magnets can be ascribed to the effects of hydrogen on the magnetic properties of the powder. It can be attributed partially at least to differences in the degree of alignment of the milled powders due to the reduced anisotropy of the $Pr_2Fe_{14}B$ phase in the HD powder. A reduction in the degree of alignment was confirmed by the results of X-ray diffraction[4]. Some additional misalignment of the c-axis in the sintered magnets would occur with a reduced remanence due to partial spin reorientation induced by hydrogen[4,11].

The significantly reduced coercivity of the magnet made from fully degassed powder might also be due to an increased oxygen content for this magnet due to the absence of hydrogen during the sintering of this material[12]. It should also be noted that the milling efficiency of the powder could be influenced by the degassing procedure and the lower coercivity of the magnets made from partially and fully degassed powder could also be due in part to an increased grain size. Studies are underway to correlate the magnetic properties with the detailed microstructures (before and after annealing). The magnetic properties of the present magnets are summarized in Table II.

Table II. Comparison of various Pr-Fe-B and Nd-Fe-B sintered permanent magnets.

Alloy Type	Processing Conditions			Br [kG]	iHc [kOe]	bHc [kOe]	(BH)max [MGOe]	SF ratio
$Pr_{16}Fe_{76}B_8$	As-sintered	HD	9h	10.1	13.6	8.9	23.9	0.62
			18h	10.9	14.9	10.2	29.4	0.77
			27h	11.0	13.2	10.0	28.6	0.79
			36h	11.1	14.3	10.1	28.8	0.75
			45h	11.4	13.9	10.6	31.2	0.84
	Annealed	HD	9h	10.4	14.4	9.8	26.2	0.79
			18h	10.9	17.5	10.5	29.2	0.81
			27h	11.2	16.7	10.9	30.8	0.89
			36h	11.2	15.3	10.7	30.8	0.81
			45h	11.5	14.9	11.1	32.1	0.93
	As-sintered	PD	18h	11.3	14.5	10.0	31.1	0.66
		TD	18h	12.0	9.9	8.4	31.8	0.73
	Annealed	PD	18h	11.8	15.2	11.6	35.2	0.93
		TD	18h	12.2	10.6	8.9	36.0	0.79
$Nd_{16}Fe_{76}B_8$	As-sintered	HD	9h	10.9	8.9	7.4	26.4	0.60
			18h	12.5	12.6	10.5	37.4	0.75
			27h	11.9	13.2	10.8	35.4	0.82
			36h	11.9	12.9	10.6	34.3	0.80
			45h	11.5	9.6	8.6	31.5	0.85
	Annealed	HD	9h	10.9	8.4	7.7	26.9	0.77
			18h	11.7	9.2	7.9	29.3	0.70
			27h	11.8	12.2	9.8	33.0	0.75
			36h	11.5	11.9	9.6	30.7	0.67
			45h	11.7	9.9	8.7	32.9	0.80

(Average error : Br ± 0.1, iHc : ±0.5, (BHmax : ±0.9)

It has been shown[13] that the degree of alignment of the c-axis affects both c and N parameters in the equation iHc = c Hn - N Ms and a better alignment yields a smaller iHc through a decrease in c, which overwhelms the effect of a reduction in N. Diminished alignment would result in a lower remanence and a higher coercivity due to the decreased internal demagnetization fields[14,15]. It has been reported[4] that there is a good linear relationship between remanence and intrinsic coercivity that holds only for (optimum) Pr-Fe-B-type magnets. Plotting Br versus iHc for the present magnets also gives a straight line relationship, as shown in fig. 8.

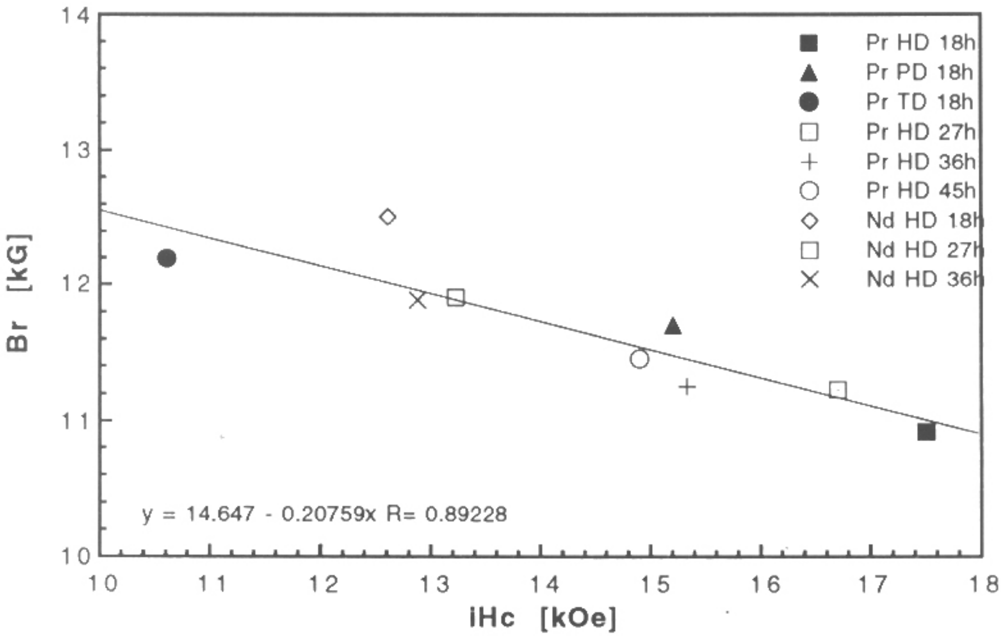

Fig. 8. Empirical correlation between Br and iHc of various annealed $Pr_{16}Fe_{76}B_8$ and as-sintered $Nd_{16}Fe_{76}B_8$ permanent magnets (optimum milling conditions).

4. Conclusions

The intrinsic coercivity of $Pr_{16}Fe_{76}B_8$ sintered magnets can be increased substantially by annealing. This post-sintering heat treatment was found to be detrimental to the magnetic properties of $Nd_{16}Fe_{76}B_8$ magnets. The loop shape improved considerably and good overall magnetic properties have been achieved in sintered magnets prepared from partially desorbed powders. It has also been shown that there is an empirical straight line relationship between remanence and intrinsic coercivity for optimum Pr-Fe-B and Nd-Fe-B HD magnets. Further studies are being carried out to optimize the procedures outlined in this paper and to correlate the magnetic behaviour with the detailed microstructures.

5. Acknowledgments

Many thanks are due to the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and CNEN (Comissão Nacional de Energia Nuclear) for the provision of a research grant (R.N.Faria). Thanks are due to REP (Rare Earth Products) for the provision of the alloys. Thanks are also due to the SERC, EURAM and CEAM (Concerted European Action on Magnets) for the support of the general research programme of which this work forms a part.

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