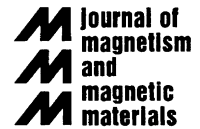




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# The influence of zirconium addition and process parameters on the magnetic properties of Pr-Fe-B sintered magnets

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## Abstract

Sintered magnets based on the compositions  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  and  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  were produced using the hydrogen decrepitation process. Sintered magnets prepared under specific processing conditions from the zirconium-free alloy exhibited excellent remanence (1.22 T), intrinsic coercivity (1.22 T) and energy product ( $278 \text{ kJm}^{-3}$ ). The squareness factor of magnets prepared from the  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  alloy was improved considerably (0.96). This investigation also shows the remarkable influence of zirconium addition on the intrinsic coercivity of these permanent magnets. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* PrFeB magnets; Zirconium addition; Hydrogen decrepitation

## 1. Introduction

Recent work has shown that addition of zirconium to Pr-based magnets, produced via the hydrogenation disproportionation, desorption, and recombination process was an effective way to develop remanence and coercivity in these materials [1]. Addition of Zr to nanocrystalline PrFeB-based magnets led to a dramatic decrease in size of the hard magnetic grains ( $<10 \text{ nm}$ ), with remarkable influence on the magnetic properties of single phase magnets [2]. Addition of Zr to sintered NdFeB permanent magnets reduced coercivity from 0.9 to  $\sim 0.6 \text{ T}$  [3]. Conversely, intrinsic coercivity of mechanically milled PrFeB powders was enhanced from  $\sim 1.6$  to  $1.8 \text{ T}$  with

the addition of Zr [4]. None of these investigations have reported about the influence of zirconium addition on the magnetic properties of PrFeB sintered magnets. In this investigation, sintered permanent magnets with compositions of  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  and  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  were prepared via the hydrogen decrepitation (HD) process. The influence of zirconium addition, sintering temperature and cooling rate from the sintering temperature on the magnetic properties of these HD magnets has been investigated.

A feature of melt-spun Nd-Fe-B alloy and mechanically alloyed Sm-Fe-N alloy is the inverse correlation between their remanence and coercivity [5]. Similar magnetic behavior has been observed in various strontium hexaferrites [6]. An empirical correlation between remanence and coercivity for Pr-based magnets that exhibited optimum magnetic properties has been reported

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[7]. In this study, magnetic properties of the  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  and  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  HD sintered magnets have been compared to those in which the inverse correlation between remanence and coercivity of PrFeB-type magnets were observed (only for  $B_r$  and  $\mu_0 i H_c \geq 1$  T). The maximum observed magnetic properties and the calculated properties of these magnets have been compared. Various Pr–Fe–B-type magnets, prepared by the standard powder metallurgy (PM) route, the HD process, hot pressing (HP), hot rolling (HR) and die upsetting (DU), have also been included for comparison.

## 2. Experimental

Two commercial alloys in the as-cast state were studied. To produce Pr-based HD magnets [8,9],  $\sim 35$  g of the cast alloy ingot was placed in a stainless steel hydrogenation vessel. This was then evacuated to backing-pump pressure. Hydrogen was introduced to a pressure of 1 bar, and this resulted in decrepitation of the bulk material. The vessel was then evacuated to backing-pump pressure for 30–40 min, the material transferred to a roller ball mill under a protective nitrogen atmosphere and milled for 20 h 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 nitrogen atmosphere. The fine powder was aligned by pulsing three times in a 4.5 T magnetic field, pressed isostatically at  $1000 \text{ kg cm}^{-2}$ , vacuum sintered for 1 h at  $1060^\circ\text{C}$  followed by slow cooling (SC) in the furnace ( $\sim 3.5^\circ\text{C min}^{-1}$ ) or fast cooling (FC) outside the furnace. For comparison, some samples were sintered at  $1100^\circ\text{C}$  for 1 h and rapidly cooled to room temperature.

Magnetic characterization of the sintered PrFeB(Zr) magnets was carried out using a permeameter. Measurements were carried out after saturation in a pulsed field of 4.5 T. In order to compare with the experimental results, the theoretical remanence of the HD magnets was estimated from the expression [10,11]

$$B_r = \langle \cos \theta \rangle f P I_s, \quad (1)$$

where  $\langle \cos \theta \rangle$  is the degree of easy-axis alignment of the  $\text{Pr}_2\text{Fe}_{14}\text{B}$  matrix phase ( $\phi$ ). It is 0.5 for an isotropic magnet and increases to 1 for a perfectly aligned magnet (good practical magnets should have  $\cos \theta$  around 0.92–0.95 [12]). The volume fraction ( $0 \leq f \leq 1$ ) of the  $\text{Pr}_2\text{Fe}_{14}\text{B}$  matrix phase in an ideal magnet is unity (to achieve high densification, practical magnets are produced with higher amounts of rare-earth and the volume fraction is maintained around 0.82–0.85). The packing factor or relative density ( $P = \text{magnet density/theoretical density}$ ) for an ideal permanent magnet is also unity (in practical magnets produced by powder metallurgy it can reach 0.96 [12]).  $I_s$  is spontaneous polarization of the  $\text{Pr}_2\text{Fe}_{14}\text{B}$  matrix phase (and is dependent on the temperature coefficient  $\beta$ ).

The spontaneous magnetization ( $M_s$ ) is given by the ratio of the magnetic moment and the volume.  $\text{Pr}_2\text{Fe}_{14}\text{B}$  has a tetragonal crystal structure with lattice constants  $a = 8.81 \times 10^{-10} \text{ m}$  and  $c = 12.27 \times 10^{-10} \text{ m}$  [13] ( $V = a^2 c = 9.52 \times 10^{-28} \text{ m}^3$ ). The magnetization in units of Bohr magnetons ( $\mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1}$ ) per formula unit at room temperature (300 K) is  $31.9 \mu_B/\text{f.u.}$  [13]. Four  $\text{Pr}_2\text{Fe}_{14}\text{B}$  formula units in a cell [14] with these dimensions gives a total magnetic moment of  $127.6 \mu_B$  ( $4 \times 31.9 \times \mu_B = 1.183 \times 10^{-21}$ ). Therefore, the spontaneous magnetization of  $\text{Pr}_2\text{Fe}_{14}\text{B}$  is  $12.42 \times 10^5 \text{ Am}^{-1}$  ( $1.183 \times 10^{-21}/9.52 \times 10^{-28}$ ). The spontaneous polarization is then 1.56 T ( $I_s = M_s \mu_0$ ;  $\mu_0 = 4\pi \times 10^{-7} \text{ T mA}^{-1}$ ). Reported spontaneous polarization for the  $\text{Pr}_2\text{Fe}_{14}\text{B}$  matrix phase is 1.56 T [15] and 1.575 T (at 293 K) [16]. The differences in these values can be attributed to the temperature coefficient of  $I_s$ . The highest remanence of a PrFeB permanent magnet (ideal) can be considered to be around 1.58 T ( $\langle \cos \theta \rangle = 1$ ,  $f = 1$  and  $P = 1$ ).

The molecular mass of  $\text{Pr}_2\text{Fe}_{14}\text{B}$  is 1074.47 g ( $2 \times 140.9 + 14 \times 55.847 + 10.811$ ) and four formula units in a cell with a volume of  $9.52 \times 10^{-28} \text{ m}^3$  resulted in theoretical density of approximately  $7.5 \text{ g cm}^{-3}$  ( $4 \times 1074.47/6.02 \times 10^{23}/9.52 \times 10^{-28} = 7.499 \text{ Mg m}^{-3}$ ). Room temperature X-ray density for  $\text{Pr}_2\text{Fe}_{14}\text{B}$  is  $7.53 \text{ g cm}^{-3}$  [17]. Previously calculated and observed densities [14] for  $\text{Pr}_2\text{Fe}_{14}\text{B}$  were 7.513 and  $7.51 \text{ g cm}^{-3}$ , respectively. The calculated

density for  $\text{Nd}_2\text{Fe}_{14}\text{B}$  has a slightly higher value ( $7.6 \text{ g cm}^{-3}$ ) [18].

### 3. Results and discussion

Table 1 shows the magnetic properties of the  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  and  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  HD magnets sintered at  $1060^\circ\text{C}/1100^\circ\text{C}$  and fast or slow cooled to room temperature. The remanence (1.22 T) of the magnet sintered at  $1100^\circ\text{C}$  and fast cooled was higher than that of the magnet sintered at  $1060^\circ\text{C}$  and slowly cooled (1.18 T). Conversely, the intrinsic coercivity of the former (1.22 T) was lower than that of the latter (1.37 T). In both cases, the density ( $\rho$ ) of the HD magnets was close to the calculated value and the packing factor, around 0.97–0.98. This high packing density is due probably to the HD process that produces a hydrogen atmosphere during sintering [19]. Similar behavior with respect to remanence and intrinsic coercivity has been previously reported for  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD sintered magnets produced with powders milled for different times [9]. It has also been reported that in the case of Sm–Co magnets, the increase in grain size, due to increase in sintering temperature, led to higher remanence values even when the density was unaffected [20,21]. Zirconium increases significantly the squareness factor (SF) at the expense of intrinsic coercivity. SC produces samples with higher intrinsic coercivity, compared to rapid cooling. Small changes in remanence of these magnets can be observed but intrinsic coercivity changed dramatically with Zr addition (and change in cooling rate).

The magnetic properties of various permanent magnets [22–30] and the HD sintered magnets studied here are compared in Table 2. The  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD magnet sintered at  $1100^\circ\text{C}$  for 1 h showed very good energy product ( $278 \text{ kJ m}^{-3}$ ) alongside a sintered permanent magnet prepared from a totally desorbed (TD) powder ( $286 \text{ kJ m}^{-3}$ ) [9], but the TD magnet showed a much lower intrinsic coercivity. Thus, the  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD sintered permanent magnet exhibited excellent overall magnetic properties. The slightly higher magnetic properties of the  $\text{Pr}_{15}\text{Fe}_{79}\text{B}_6$  magnet [23]

Table 1  
Magnetic properties of  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  and  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  HD sintered magnets

| Alloy   | Sintering temperature-cooling rate | $B_r$ (T)<br>( $\pm 0.02$ ) | $\mu_0 H_c$ (T)<br>( $\pm 0.02$ ) | $\mu_0 H_c$ (T)<br>( $\pm 0.02$ ) | SF (ratio)<br>( $\pm 0.02$ ) | $(BH)_{\text{max}}$<br>( $\text{kJ m}^{-3}$ ) ( $\pm 5$ ) | $\rho$ ( $\text{g cm}^{-3}$ )<br>( $\pm 0.03$ ) |
|---|------------------------------------|-----------------------------|-----------------------------------|-----------------------------------|------------------------------|---|---|
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$                  | $1100^\circ\text{C}$ -FC           | 1.22                        | 1.22                              | 1.06                              | 0.82                         | 278   | 7.39  |
| $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$ | $1060^\circ\text{C}$ -FC           | 1.20                        | 0.67                              | 0.66                              | 0.96                         | 266   | 7.33  |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$                  | $1060^\circ\text{C}$ -SC           | 1.18                        | 1.37                              | 1.10                              | 0.80                         | 254   | 7.35  |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$                  | $1060^\circ\text{C}$ -FC           | 1.16                        | 1.21                              | 0.93                              | 0.68                         | 253   | 7.34  |
| $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$ | $1060^\circ\text{C}$ -SC           | 1.12                        | 1.02                              | 0.86                              | 0.61                         | 227   | 7.35  |

Table 2  
Magnetic properties of various Pr-based magnets [19–27]

| Alloy  | Proc. route | $B_r$ (T) | $\mu_0 i H_c$ (T) | $(BH)_{\max}$ ( $\text{kJ m}^{-3}$ ) | $B_r^2/4\mu_0$ ( $\text{kJ m}^{-3}$ ) | Refs.     |
|--|-------------|-----------|-------------------|--------------------------------------|---------------------------------------|-----------|
| Magnet type I (Heat-treated)   |             |           |                   |                                      |                                       |           |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | TD          | 1.22      | 1.06              | 286                                  | 296                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.22      | 1.22              | 278                                  | 296                                   | This work |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.20      | 1.31              | 268                                  | 286                                   | [22]      |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.18      | 1.37              | 254                                  | 277                                   | This work |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | PD          | 1.18      | 1.52              | 280                                  | 277                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.15      | 1.49              | 255                                  | 263                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.12      | 1.67              | 245                                  | 250                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.12      | 1.53              | 245                                  | 250                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$                          | HD          | 1.12      | 1.02              | 227                                  | 250                                   | This work |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.09      | 1.75              | 232                                  | 236                                   | [9]       |
| $\text{Pr}_{16.9}\text{Fe}_{79.1}\text{B}_4$                                       | HD          | 1.06      | 2.03              | 201                                  | 223                                   | [8]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$ (9 h, undermilled)                        | HD          | 1.04      | 1.44              | 208                                  | 215                                   | [9]       |
| $\text{Pr}_{15}\text{Fe}_{62.5}\text{Co}_{16}\text{Al}_1\text{B}_{5.5}$            | PM          | 1.27      | 0.96              | 302                                  | 321                                   | [23]      |
| $\text{Pr}_{17}\text{Fe}_{76.5}\text{B}_5\text{Cu}_{1.5}$                          | HP          | 1.26      | 1.00              | 288                                  | 316                                   | [24]      |
| $\text{Pr}_{14}\text{Dy}_1\text{Fe}_{62.5}\text{Co}_{16}\text{Al}_1\text{B}_{5.5}$ | PM          | 1.23      | 1.15              | 275                                  | 301                                   | [25]      |
| $\text{Pr}_{14}\text{Tb}_1\text{Fe}_{62.5}\text{Co}_{16}\text{Al}_1\text{B}_{5.5}$ | PM          | 1.18      | 1.38              | 258                                  | 277                                   | [25]      |
| $\text{Pr}_{13}\text{Dy}_2\text{Fe}_{62.5}\text{Co}_{16}\text{Al}_1\text{B}_{5.5}$ | PM          | 1.15      | 1.43              | 256                                  | 263                                   | [25]      |
| $\text{Pr}_{13}\text{Tb}_2\text{Fe}_{62.5}\text{Co}_{16}\text{Al}_1\text{B}_{5.5}$ | PM          | 1.13      | 1.52              | 248                                  | 254                                   | [25]      |
| $\text{Pr}_{12}\text{Dy}_3\text{Fe}_{62.5}\text{Co}_{16}\text{Al}_1\text{B}_{5.5}$ | PM          | 1.12      | 1.71              | 243                                  | 249                                   | [25]      |
| $\text{Pr}_{17}\text{Fe}_{76.5}\text{B}_5\text{Cu}_{1.5}$                          | HR          | 1.10      | 1.62              | 226                                  | 241                                   | [26]      |
| $\text{Pr}_{20.5}\text{Fe}_{73.8}\text{B}_{3.7}\text{Cu}_2$                        | HD          | 1.07      | 1.98              | 198                                  | 228                                   | [8]       |
| $\text{Pr}_{11}\text{Dy}_4\text{Fe}_{62.5}\text{Co}_{16}\text{Al}_1\text{B}_{5.5}$ | PM          | 1.04      | 2.20              | 209                                  | 215                                   | [25]      |
| $\text{Pr}_{19}\text{Fe}_{74.5}\text{B}_5\text{Cu}_{1.5}$                          | HP          | 0.99      | 1.10              | 191                                  | 195                                   | [27]      |
| Magnet type II (As-sintered)   |             |           |                   |                                      |                                       |           |
| $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$                          | HD          | 1.20      | 0.67              | 266                                  | 286                                   | This work |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | TD          | 1.20      | 0.99              | 253                                  | 286                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | PM          | 1.19      | 1.10              | —                                    | 282                                   | [28]      |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.17      | 1.23              | 255                                  | 272                                   | [22]      |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.16      | 1.21              | 253                                  | 268                                   | This work |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.14      | 1.39              | 248                                  | 258                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | PD          | 1.13      | 1.45              | 247                                  | 254                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.11      | 1.43              | 229                                  | 245                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.10      | 1.32              | 228                                  | 241                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$   | HD          | 1.09      | 1.49              | 234                                  | 236                                   | [9]       |
| $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$ (9 h, undermilled)                        | HD          | 1.01      | 1.36              | 190                                  | 203                                   | [9]       |
| Magnet type III  |             |           |                   |                                      |                                       |           |
| $\text{Pr}_{15}\text{Fe}_{79}\text{B}_6$   | PM          | 1.29      | 1.24              | 314                                  | 331                                   | [23]      |
| $\text{Pr}_{13.75}\text{Fe}_{80.25}\text{B}_6$                                     | DU          | 1.24      | 1.57              | 289                                  | 306                                   | [29]      |
| $\text{Pr}_{14}\text{Tb}_1\text{Fe}_{79}\text{B}_6$                                | PM          | 1.23      | 1.66              | 267                                  | 301                                   | [30]      |

can be attributed to the lower rare earth and boron content in this material.

Fig. 1 shows the maximum observed remanence as a function of rare earth content for various PrFeB-type permanent magnets. In general, remanences tend to be lower for magnets with higher

rare earth content, although some scatter can be seen. The high remanence value of the hot pressed magnet  $\text{Pr}_{17}\text{Fe}_{76.5}\text{B}_5\text{Cu}_{1.5}$  can be attributed to the “squeezing out” of the praseodymium-rich material during the HP operation. The saturation polarization of an alloy can be calculated as the

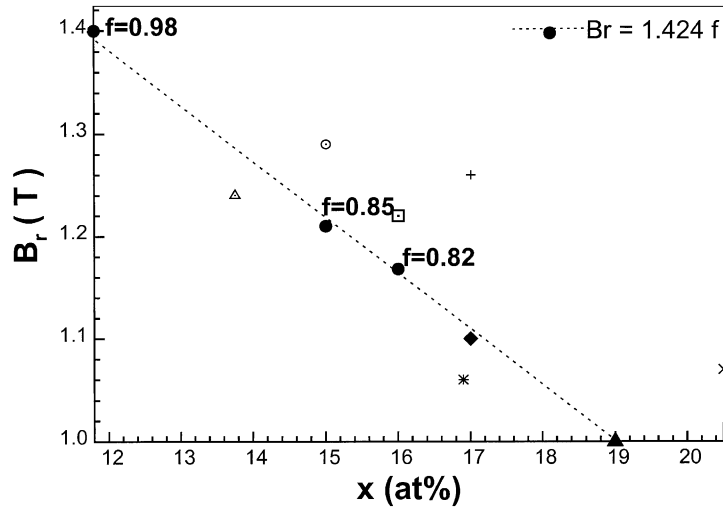


Fig. 1. Maximum remanence obtained for various Pr-based permanent magnets as a function of rare-earth content (Please refer to Table 2 to identify the alloy).

product of the volume fraction ( $f$ ) of the matrix phase present in the alloy and the spontaneous polarization of the  $\text{RE}_2\text{Fe}_{14}\text{B}$  matrix phase ( $f I_s$ ) [31]. The reported volume fraction of the matrix phase in  $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$  alloy is 0.82 and in  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  sintered magnet is 0.85. Assuming the same volume fraction of  $\phi$  in Pr-based magnets (and alloys), and that a stoichiometric magnet ( $\text{Pr}_{11.8}\text{Fe}_{82.3}\text{B}_{5.9}$  or  $\text{Pr}_2\text{Fe}_{14}\text{B}$ ) has a matrix phase volume fraction of 0.98 (upper limit that can be achieved in practice [32]), a plot can be drawn to roughly estimate remanence as a function of the alloy volume fraction. Fig. 1 also shows the calculated remanences for good permanent magnets (assuming:  $\langle \cos \theta \rangle f P I_s = 0.92 \times f \times 0.98 \times 1.58 = 1.424f$ ) with volume fractions of 0.98 (hypothetical), 0.85 and 0.82. The remanence of a magnet with 16 at% of praseodymium should be around 1.168 T. This agrees well with the average value (1.176 T) obtained for  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD sintered permanent magnets studied here. For a  $\text{Pr}_{15}\text{Fe}_{77}\text{B}_8$  ( $f = 0.85$ ) magnet,  $B_r$  would be 1.21 T.

The intrinsic coercivity ( $\mu_0 iH_c$ ) of sintered  $\text{Pr}_{15}\text{Fe}_{77}\text{B}_8$  permanent magnets at room temperature can be described by [16]

$$\mu_0 iH_c = c\mu_0 H_A - N I_s, \quad (2)$$

where the magnetocrystalline anisotropy field ( $\mu_0 H_A$ ) for the matrix phase is 9.15 T ( $7.28 \text{ MA m}^{-1}$ ) and  $c$  and  $N$  are the microstructural factors for the sintered magnet [16]. In a well-aligned  $\text{Pr}_{15}\text{Fe}_{77}\text{B}_8$  sintered magnet (degree of alignment = 0.92) the reported microstructural parameters  $c$  and  $N$  are equal to 0.38 and 1.1, respectively. According to Hirose and Tsubokawa [16] the degree of alignment of the  $c$ -axis affects both parameters,  $c$  and  $N$ . Improved alignment yields a smaller intrinsic coercivity through decrease in  $c$ , which surpasses the effect of reduction in  $N$ . The post-sintering heat treatment makes  $N$  smaller than in the as-sintered state and  $c$  does not change with this treatment. In the  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD sintered magnets studied here, slow cooling can be considered as the post-sintering heat treatment and it produces improved isolation of the matrix phase (yielding better intrinsic coercivity). Hence, in the present magnets, the  $c$  factor should remain constant and  $N$  in the slowly cooled magnets should be smaller than in the fast cooled magnets. Substituting Eq. (1) in (2):

$$\mu_0 iH_c = c\mu_0 H_A - (NB_r / \langle \cos \theta \rangle f P). \quad (3)$$

The slow and fast cooled  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD sintered magnets studied here have a relative density of

98% ( $P = 0.98$ ) and a volume fraction of around 82% ( $f = 0.82$ ). Assuming a degree of  $c$ -axis alignment and  $c$  factor identical to those reported for the  $\text{Pr}_{15}\text{Fe}_{77}\text{B}_8$  sintered magnets ( $\langle \cos \theta \rangle = 0.92$  and  $c = 0.38$ ), the parameter  $N$  can be determined for the  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD magnets ( $N = (3.48 - \mu_0 iH_c)/1.353 B_r$ ). The remanence and coercivity of the fast cooled HD  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  magnets are 1.16 T and 1.21 T (1060°C), respectively, and  $N = 1.45$ . For the slowly cooled HD magnets,  $N = 1.32$  since  $B_r = 1.18$  T and  $\mu_0 iH_c = 1.37$  T, confirming the expected reduction in this parameter with post-sintering heat treatment. Since no significant change in remanence with Zr addition has been observed in these HD magnets, a significant change in microstructural factors probably occurs, in view of the observed dramatic decrease in coercivity. This is surprising as Zr-addition is known to increase the anisotropy field of PrFeB compounds [33] and according to Eq. (2), an increase in  $iH_c$ .

Fig. 2 shows calculated and experimental values of remanence and intrinsic coercivity of various Pr-based permanent magnets. There is a decreasing monotonic behavior for heat-treated magnets (type I), independent of composition, additions and processing route. Coercivities of the magnets

in the as-sintered condition (type II) are not fully developed to permit a good curve fit and type III magnets shift to higher  $B_r$  values. Zirconium addition has so much influence in these Pr-based HD magnets that no curve fitting has been possible for these samples. A data point for a  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  sintered magnet (reported in Ref. [9]) lies far away from the trend shown by most of the other data. The reason for this outlying point is the short milling time (9 h) used for processing this HD magnet (undermilling yields magnets with large polycrystal grains). Also included in this graph is the calculated value of coercivity (1.74 T) using Eq. (3) for a hypothetical  $\text{Pr}_{15}\text{Fe}_{77}\text{B}_8$  magnet with  $B_r = 1.21$  T (employing microstructural parameters  $c = 0.38$  and  $N = 1.1$  [16];  $\langle \cos \theta \rangle = 0.92$ ,  $f = 0.85$ ,  $P = 0.98$  and  $\mu_0 iH_c = 3.48 - 1.435 B_r$ ). The calculated value of coercivity for another hypothetical  $\text{Pr}_{15}\text{Fe}_{77}\text{B}_8$  permanent magnet with an inferior degree of easy axis alignment (0.86) and a  $B_r = 1.13$  T ( $c = 0.39$  and  $N = 1.11$  [16];  $f = 0.85$ ,  $P = 0.98$  and  $\mu_0 iH_c = 3.57 - 1.549 B_r$ ) is about 1.82 T.

Calculated values of the theoretical upper limit (for  $bH_c \geq 0.5 B_r$ ) of the energy product ( $B_r^2/4\mu_0$ ) have been included in Table 2. Fig. 3 shows the experimental values of energy product and  $iH_c$  for

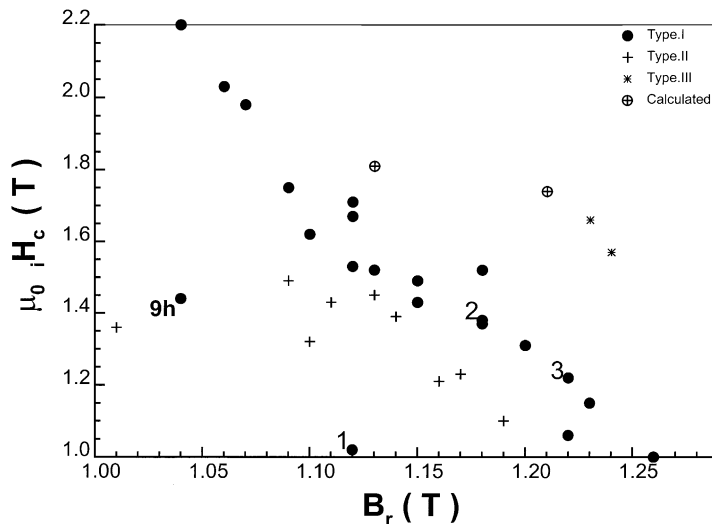


Fig. 2. Calculated and experimental values of remanence and coercivity of various Pr-based magnets (1:  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  sintered at 1060°C/SC, 2:  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  sintered at 1060°C/SC and 3:  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  sintered at 1100°C/FC).

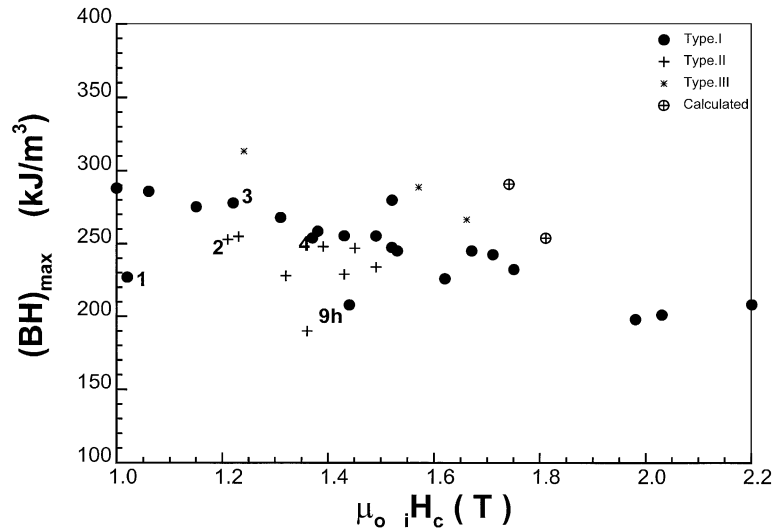


Fig. 3. Energy product and intrinsic coercivity of various Pr-based permanent magnets (1:  $\text{Pr}_{16}\text{Fe}_{75.5}\text{B}_8\text{Zr}_{0.5}$  /1060°C/SC, 2:  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$ /1060°C/FC, 3:  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  /1100°C/FC and 4:  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  /1060°C/SC).

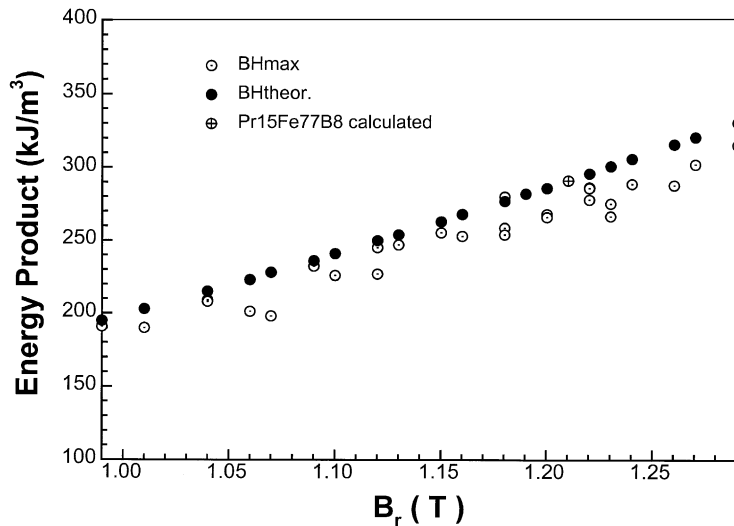


Fig. 4. Calculated and experimental values of energy product and remanence of various Pr-based permanent magnets.

the Pr-based magnets. Fig. 4 shows  $B_r^2/4\mu_0$ ,  $(\text{BH})_{\text{max}}$  and  $B_r$  for the Pr-based magnets. The calculated energy product ( $291 \text{ kJ m}^{-3}$ ) for the  $\text{Pr}_{15}\text{Fe}_{77}\text{B}_8$  magnet (with a remanence of 1.21 T and a calculated intrinsic coercivity of 1.76 T) has also been included. There is good agreement

between these parameters and, as expected, the theoretical energy product is always higher than the measured  $(\text{BH})_{\text{max}}$ . Practical Pr-based magnets can be improved by increasing the volume fraction and degree of alignment to 0.95 and if the relative density is decreased to only 0.95 (by decreasing the

amount of RE), the remanence could reach 1.355 T and the energy product  $365 \text{ kJ m}^{-3}$ . It has been possible to sinter high-energy magnets with Nd content as low as 13 at% [34]. The degree of alignment in  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD magnets, determined by X-ray diffraction (pole figure), varies from 88% to 97% (according to milling time) [35].

$\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$  HD sintered magnets showed much less tolerance to sintering at temperatures higher than  $1050^\circ\text{C}$  and a dramatic decrease in the intrinsic coercivity [36]. The excellent magnetic properties of the  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD magnets sintered at  $1100^\circ\text{C}$  are in agreement with data reported recently which showed that Pr- and Nd-based magnets have a different grain growth mechanism. Pr-based magnets withstand high temperature annealing without grain growth [21]. Evidence of significantly reduced crystal alignment, in the case of annealed  $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$  magnets, has also been found.

#### 4. Conclusions

In this investigation  $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$  HD magnet (sintered at  $1100^\circ\text{C}$  for 1 h) with excellent properties ( $B_r = i H_c = 1.22 \text{ T}$ ,  $\text{SF} = 0.82$ ,  $\text{BH}_{\text{max}} = 278 \text{ kJ m}^{-3}$  and  $\rho = 7.4 \text{ g cm}^{-3}$ ) has been produced. In rapidly cooled specimens sintered at  $1060^\circ\text{C}$ , zirconium increased the SF (from 0.68 to 0.96) and remanence (from 1.16 to 1.20 T), at the expense of intrinsic coercivity. Sintering at higher temperature ( $1100^\circ\text{C}$ ) had the same effect on SF (increased from 0.68 to 0.82) without affecting intrinsic coercivity. The magnetic properties of the Zr-free magnets only were in good agreement with the inverse correlation between remanence and coercivity of Pr-based magnets. Good agreement between calculated and observed magnetic properties has been achieved in PrFeB-type permanent magnets. Further studies are being carried out to optimize the amount of zirconium added to the alloy and the sintering temperature.

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