Praseodymium-based HD-sintered magnets produced using a mixture of cast alloys

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Abstract

Magnetic alloys based on the compositions $Pr_{16}Fe_{75.5}B_8Zr_{0.5}$, $Pr_{13}Fe_{80.5}B_6Zr_{0.5}$ and $Pr_{12.6}Fe_{68.7}Co_{11.6}B_6Zr_{0.5}Ga_1$ have been employed in the present investigation. The hydrogen decrepitation (HD) process was used to produce sintered permanent magnets using a mixture of these alloys, in equal proportions. Standard magnets with compositions $Pr_{16}Fe_{76}B_8$, $Pr_{16}Fe_{75.5}B_8Zr_{0.5}$, $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ and $Pr_{20}Fe_{74}B_4Cu_2$ have also been included in this work for a comparison. A dramatic influence of additions on the magnetic properties of these Pr-based magnets has been shown. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In the past, power blending has been employed to prepare sintered permanent magnets. A recent study [1] gives a brief review on studies that employed this process to produce sintered magnets and also reports that it has been used successfully to produce Nd–Fe–B magnets with Co addition. The main advantage is that it allows the composition, and hence magnetic properties, of the sintered magnets to be adjusted, subsequent to casting of basic alloys [1]. Recently, it has been reported that adding Zr to nanocrystalline PrFeB-based magnets led to a dramatic decrease in the size of hard magnetic grains (<10 nm), with a remarkable influence on the magnetic properties of single phase magnets [2]. It has been shown that copper additions on Pr-based HD-sintered magnets also have great influence on their magnetic properties [3]. In the present work, Pr-based HD magnets prepared using a combination of two alloys have been investigated. The influence of zirconium, gallium, copper and cobalt additions on their magnetic properties has been studied. Standard Pr-based HD-sintered magnets of well-known compositions (with and without zirconium and copper additions) have also been included in the present work as a reference.

2. Experimental

Four commercial Pr-based alloys in the as-cast state were used in this study. To produce the standard HD-sintered magnets [4–6], 35 g of the bulk ingot were placed in a stainless-steel hydrogenation vessel, which was then evacuated to

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backing-pump pressure. In order to produce a magnet from two alloys with distinct compositions, 17.5 g of each cast alloy were placed together in the hydrogenation vessel. Hydrogen was introduced to a pressure of 1 bar, which resulted in decrepitation of the bulk material. This material was evacuated to backing-pump pressure for 30–40 min and then transferred to a roller ball mill under a protective nitrogen atmosphere. Next, it was 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 a nitrogen atmosphere. The fine powder was aligned by pulsing 3 times to a 4.5 T magnetic field, pressed isostatically at $1000 \, \text{kg/cm}^2$ and then vacuum sintered for 1 h at 1060°C, followed by fast cooling outside the furnace. To evaluate the effect of additions only on sintering, no post-sintering heat treatment was carried out. Magnetic measurements of the HD-sintered magnets were performed in a permeameter after saturation in a pulsed field of 4.5 T.

3. Results and discussion

Table 1 shows the magnetic properties of the Pr-based HD magnets sintered at 1060°C for 1 h and fast cooled to room temperature. A magnet with a mean composition of $Pr_{14.5}Fe_{78}B_7Zr_{0.5}$ prepared using a mixture of two alloys, $Pr_{16}Fe_{75.5}B_8Zr_{0.5}$ and $Pr_{13}Fe_{80.5}B_6Zr_{0.5}$, exhibited the best remanence (1.23 T) and energy product ($277 \, \text{kJ/m}^3$). A comparison between the magnetic properties of this HD-sintered permanent magnet and the

$Pr_{14.3}Fe_{72.1}Co_{5.8}B_7Zr_{0.5}Ga_{0.5}$ (mean composition) magnet, produced using a mixture of $Pr_{16}Fe_{75.5}B_8Zr_{0.5}$ and $Pr_{12.6}Fe_{68.7}Co_{11.6}B_6Zr_{0.5}Ga_1$ alloys, shows that Co and/or Ga addition increases the coercivity but decreases B_r, $(BH)_{max}$ and squareness factor (SF). The $Pr_{16}Fe_{76}B_8$ magnet exhibited the highest intrinsic coercivity (1.21 T). This coercivity can be further increased with a post-sintering heat treatment [7]. Zirconium addition had the effect of increasing significantly SF at the expenses of the intrinsic coercivity, in both magnets ($Pr_{16}Fe_{75.5}B_8Zr_{0.5}$ and $Pr_{14.5}Fe_{78}B_7Zr_{0.5}$). Copper containing magnets exhibited low-energy product but this can be attributed partially to the higher Pr-content in these magnets. It has been shown [8] that after a post-sintering heat treatment high coercivity can be achieved in Cu-containing magnets. Copper is indispensable in hot pressed and hot-rolled magnets [9,10] and improves corrosion resistance [11]. A comparison of magnetic properties of various permanent magnets found in the literature [7,12,13] and that of HD-sintered magnets used in this investigation is given in Table 2.

The mean density of the HD-sintered praseodymium-based magnets was around $7.31 \, \text{g/cm}^3$. The molecular mass of $Pr_2Fe_{14}B$ is 1074.47 g and four formula units in a cell of $9.52 \times 10^{-28} \, \text{m}^3$ give a theoretical density of approximately $7.50 \, \text{g/cm}^3$ [14,15]. Previously, calculated and observed densities for $Pr_2Fe_{14}B$ were 7.513 and $7.51 \, \text{g/cm}^3$, respectively [14]. Room temperature X-ray density for $Pr_2Fe_{14}B$ is $7.53 \, \text{g/cm}^3$ [16]. The excellent relative density ($\sim 97\%$ or 7.3/7.5) obtained in the present magnets is probably due to the HD

Table 1
Magnetic properties of Pr-based HD magnets in the as-sintered condition

Magnet composition (at%)	B_r (T) (± 0.02)	$\mu_0 \, {}_iH_c$ (T) (± 0.02)	$\mu_0 \, {}_bH_c$ (T) (± 0.02)	$\mu_0 \, H_k$ (T) (± 0.02)	$SF = H_k/{}_iH_c$ (ratio)	$(BH)_{max}$ (kJ/m^3) (± 5)	$B_r\mu_0 \, {}_bH_c/4$ (kJ/m^3)	$B_r^2/4\mu_0$ (kJ/m^3)	Density (g/cm^3) (± 0.03)
$Pr_{14.3}Fe_{72.1}Co_{5.8}B_7Zr_{0.5}Ga_{0.5}$	1.20	0.92	0.78	0.65	0.70	261	234	286	7.27
$Pr_{14.5}Fe_{78}B_7Zr_{0.5}$	1.23	0.72	0.68	0.65	0.90	277	209	301	7.35
$Pr_{16}Fe_{75.5}B_8Zr_{0.5}$	1.19	0.67	0.66	0.64	0.96	266	196	282	7.33
$Pr_{17}Fe_{76.5}B_5Cu_{1.5}$	1.08	0.64	0.54	0.41	0.64	175	146	232	7.32
$Pr_{20}Fe_{74}B_4Cu_2$	0.90	1.20	0.70	0.48	0.40	127	157	161	7.30
$Pr_{16}Fe_{76}B_8$	1.16	1.21	0.94	0.82	0.68	253	273	268	7.31

Table 2
Magnetic properties of various $Pr_{16}Fe_{76}B_8$ magnets (as-sintered condition)

Proc. route milling time	B_r (T)	$\mu_0 {}_i H_c$ (T)	$\mu_0 {}_b H_c$ (T)	$\mu_0 H_k$ (T)	$SF = H_k/{}_i H_c$ (ratio)	$(BH)_{max}$ (kJ/m^3)	$B_r \mu_0 {}_b H_c/4$ (kJ/m^3)	$B_r^2/4\mu_0$ (kJ/m^3)	Ref.
TD—18 h	1.20	0.99	0.84	0.72	0.73	253	252	286	[7]
PM	1.19	1.10	—	—	—	—	—	282	[12]
HD—20 h	1.17	1.23	0.98	0.90	0.73	255	287	272	[13]
HD—20 h	1.16	1.21	0.94	0.82	0.68	253	273	267	This work
HD—45 h	1.14	1.39	1.06	1.17	0.84	248	302	258	[7]
PD—18 h	1.13	1.45	1.00	0.96	0.66	247	283	254	[7]
HD—36 h	1.11	1.43	1.01	1.07	0.75	229	280	245	[7]
HD—27 h	1.10	1.32	1.00	1.04	0.79	228	286	240	[7]
HD—18 h	1.09	1.49	1.02	1.15	0.77	234	278	236	[7]
HD—9 h	1.01	1.36	0.89	0.84	0.62	190	225	203	[7]
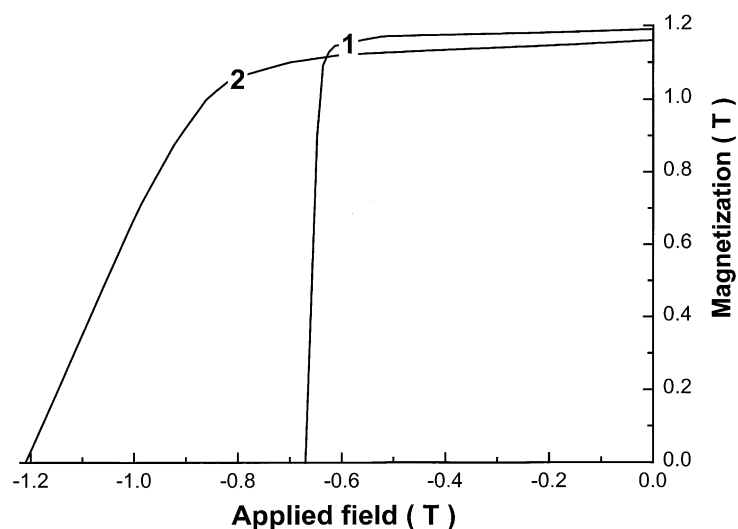
Fig. 1. Second quadrant demagnetization curves of $Pr_{16}Fe_{75.5}B_8Zr_{0.5}$ (1) and $Pr_{16}Fe_{76}B_8$ (2) HD-sintered magnets.

process that produces a hydrogen atmosphere during sintering [17].

Fig. 1 shows the demagnetization curves of $Pr_{16}Fe_{75.5}B_8Zr_{0.5}$ and $Pr_{16}Fe_{76}B_8$ HD-sintered magnets. Clearly, the addition of zirconium has a dramatic effect on their magnetic properties. A small increase in the remanence and an excellent squareness (0.96) were obtained with the addition of Zr, but, unfortunately, the intrinsic coercivity decreased dramatically with only 0.5 at% of this element in the alloy. Fig. 2 shows the maximum

remanence according to the rare earth content of the various PrFeB-type permanent magnets. As expected, remanences are lower for the magnets with higher rare-earth content. A remanence of 1.26 T has been reported for a hot pressed $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ magnet (not included in Fig. 2) [18]. This excessive high value of remanence can be attributed to the "squeezing out" of the praseo-dymium-rich material during the hot-pressing operation. According to Fig. 2 the expected value of remanence (extrapolated) for a magnet with
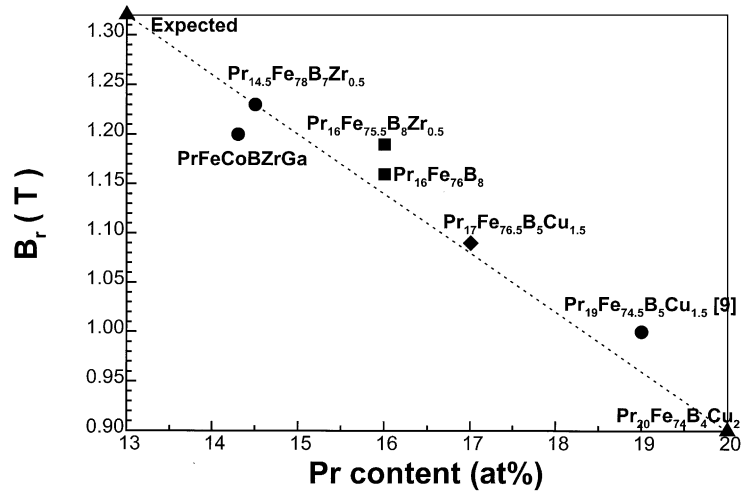
Fig. 2. Remanence of various Pr-based permanent magnets according to rare-earth content (other magnetic properties are given in Table 2).
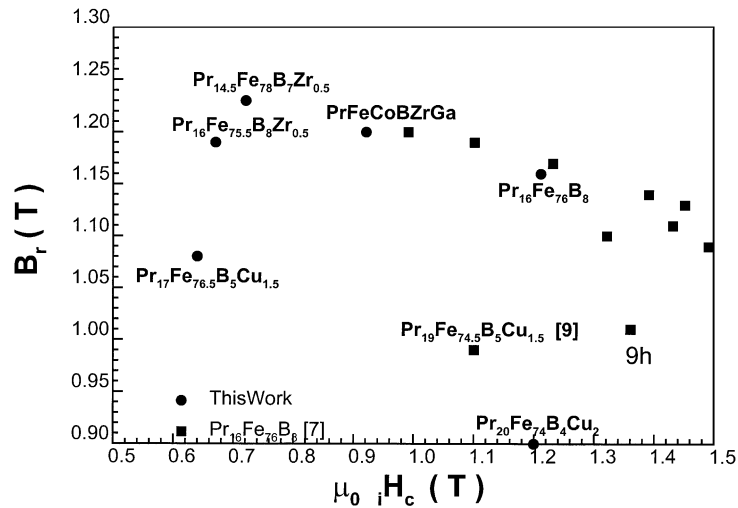

Fig. 3. Remanence and intrinsic coercivity of the present Pr-based permanent magnets compared to reported magnets, also in the as-sintered condition.

13 at% of Pr would be approximately 1.32 T. Thus, the final Pr-content of this hot-pressed magnet should be around 14 at% (loss of 3 at % of praseodymium).

Fig. 3 shows the remanence and coercivity values for the present magnets and previously reported magnets, all in the as-sintered condition. In general, the remanence decreases as the coercivity increases. This trend has also been observed after a post-sintering heat treatment in Pr-based magnets [7]. The addition of Cu to these Pr-based magnets led to deviation from this trend.
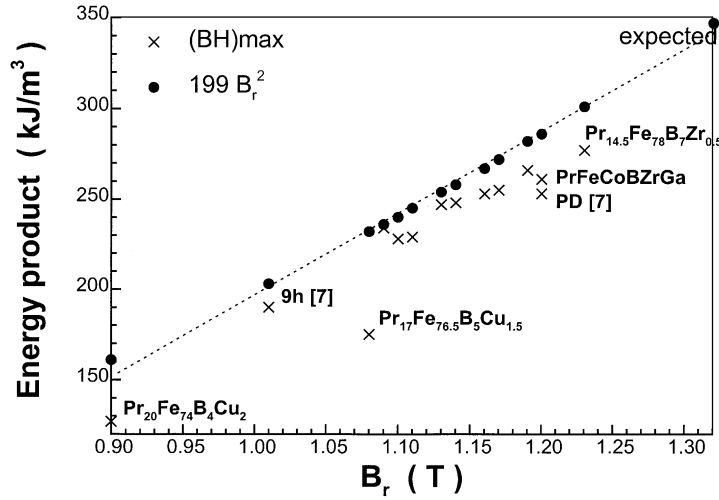
Fig. 4. Energy product of various Pr-based permanent magnets according to rare-earth content (other magnetic properties are given in Table 2).

A magnet prepared using a very short milling time (9 h) also showed a deviation from the expected trend. Undermilling yields permanent magnets with large polycrystal grains with anomalous behavior.

Fig. 4 shows values of remanence and maximum energy product for the present magnets and magnets previously reported (in the as-sintered condition). The theoretical energy product ($B_r^2/4\mu_0$) has been included for a comparison (valid if $_bH_c \geqslant 0.5B_r$) [19]. Evident disparity between $(BH)_{max}$ and $B_r^2/4\mu_0$ is found in Cu-containing magnets, and also in Zr and ZrGaCo-containing magnets. Maximum possible recoil energy ($E_{rec,max} = B_r \mu_0 {}_bH_c/4$) [19] is also given in Tables 1 and 2.

In this work, magnets with superior remanences were produced by mixing an alloy near the stoichiometric composition with another alloy which has the composition of the liquid phase during sintering. The remanence of a permanent magnet depends directly on the volume fraction (f) and saturation polarization (l_s) of hard magnetic phase (ϕ), as well as on the degree of easy-axis alignment of the single crystals ϕ grains ($\langle \cos\theta \rangle$) and magnet density. The remanence can be estimated from the expression [20,21]:

$$B_r = \langle \cos\theta \rangle f P l_s. \tag{1}$$

The degree of alignment is 0.5 for an isotropic magnet and increases to 1 for a perfectly aligned magnet. In practice, good magnets should have $\langle \cos\theta \rangle$ around 0.92–0.95 [22]. The volume fraction ($0 \leqslant f \leqslant 1$) of the matrix phase in an ideal magnet is unity. To achieve high densification, sintered magnets are produced with higher amounts of rare earth and the volume fraction of the matrix phase is maintained around 0.82–0.85. The packing factor for an ideal magnet is also unity (P = magnet density/theoretical density) and in sintered magnets it can reach 0.96 [22]. The spontaneous polarization of $Pr_2Fe_{14}B$ is 1.56 T [23]. Thus, increasing the volume fraction of the matrix phase by mixing an alloy richer in rare earth with an alloy having near stoichiometric composition increases the remanence of the sintered magnet. Since the energy product is proportional to the square of remanence, a substantial improvement is obtained in this magnetic property. Further studies are underway to correlate the magnetic behavior with the microstructure.

4. Conclusions

Mixing cast alloys of the so-called "neomax" composition and alloys with near stoichiometric composition is an efficient way of increasing the remanence and hence energy product of Pr-based magnets. Zirconium addition (0.5 at%) had the effect of increasing the squareness factor of the Pr–Fe–B HD-sintered magnet, but at the expenses of the intrinsic coercivity. In the as-sintered condition, copper had no beneficial effect on the magnetic properties of sintered magnets. Cobalt and/or gallium addition improves somewhat the intrinsic coercivity. The increase in the energy product of the magnets produced using a mixture of cast alloys has been attributed to the increase in the volume fraction of the $Pr_2Fe_{14}B$ matrix phase.

Acknowledgements

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