The Influence of Al, Cu and P Content on the Magnetic Properties of PrFeCoBNb-based HDDR Magnets

M. C. L. Oliveira, H. Takiishi, I. Costa and R. N. Faria
Instituto de Pesquisas Energéticas e Nucleares,IPEN-CNEN
S. Paulo, Brazil; e-mail: takiishi@net.ipen.br

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Abstract: This paper reports the results of investigations carried out to determine the magnetic properties of some praseodymium-based magnets represented by the formula $Pr_{14}Fe_{63.9-x}Co_{16}B_6Nb_{0.1}M_x$. Bonded magnets of various compositions were prepared from annealed alloys using the hydrogenation, disproportionation, desorption and recombination (HDDR) process. The HDDR powders were isostatically pressed and bonded with cyanoacrylate adhesive to form permanent magnets. The effect of the addition element content on the magnetic properties of these magnets was investigated. The amount of Al, Cu and P addition has a significant effect on the magnetic behavior of these magnets. Under the present processing condition 0.3 at%Al enhanced the intrinsic coercivity to 1.27 T and 0.1 at% P improved the remanence to 0.77 T. Copper addition was deleterious to the magnetic properties of the HDDR bonded magnets, independently on the content added.

Introduction

Bonded magnet powders prepared by the hydrogenation, disproportionation, desorption and recombination (HDDR) process are high coercivity materials and these can be obtained by exposing rare earth-based alloys to hydrogen at elevated temperatures (examples in [1-10]). Bonded praseodymium-based HDDR magnets are easy to produce with a relatively straightforward HDDR treatment [11-17]. It has been shown that a number of additions (Co, Zr, Nb, Ga and Dy) can considerably influence the magnetic properties of praseodymium based HDDR bonded magnets [13]. This paper reports the results of further work carried out with $Pr_{14}Fe_{63.9-x}Co_{16}B_6Nb_{0.1}M_x$ bonded HDDR magnets (M= Al, P, Cu, x = 0-1). This investigation was undertaken to study the influence of the addition content on the magnetic properties. Simultaneous additions of Al, Si, Cu, Ga and Gd have also been investigated in this work.

Experimental Procedure

Various commercial alloys in the homogenised state were studied. As per the supplier's specification, the alloys contain neodymium (0.2-0.7 wt %), aluminium (0.02-0.2 wt %) and silicon (0.01-0.04 wt %) as impurities. The chemical analyses of the as-cast alloys showed that only the phosphorous amount was below the specified or nominal composition. Homogenisation was carried out in vacuum at 1100°C for 20 h. The following procedure was used to produce the Pr-based bonded magnets via the HDDR process [11-20]. The annealed alloys were crushed into coarse lumps and 8 g batches were placed in the HDDR reactor. This reactor was then evacuated to the backing-pump pressure (~10^{-1} mbar) and hydrogen introduced until the pressure reached 0.097 MPa. The temperature of the reactor was held at 100°C for 30 minutes to allow the hydrogen decrepitation (HD) reaction to go to completion. The reactor was then heated to 770 ^{o}C at 15 ^{o}C/min and up to the desorption temperature (860 ^{o}C) at 5^{o}C/min, with a dwell time of 15 min prior to desorption [11]. Subsequent desorption and recombination was carried out under vacuum at the same temperature until a pressure of 10^{-1} mbar was reached (<10 min). Rapid cooling of the material was carried out by removing the furnace from the HDDR reactor and by coupling a water-cooled copper coil to the reactor tube. The resultant powder was crushed in air until all the material passed through a <75 μm sieve. The fine powder was subsequently encapsulated in a small cylindrical rubber bag, pulsed in a magnetic field of 6 T and pressed isostatically at 200 MPa (isotropic magnets were pressed without pulsing). The resultant green compacts were consolidated by immersion (vacuum impregnated) in low viscosity cyanoacrylate adhesive (3 Pa s) at 70^{o}C. The bonded sample was then allowed to cool to room temperature and the excess material removed to yield a cylindrical magnet (ρ= 5.0±0.3 g cm^{-3}). Magnetic characterisation of the HDDR magnets was carried out using a permeameter (accuracy: 2%). Measurements were made after saturation in a pulsed field of 6 T. Remanence values have been normalized assuming 100% density (7.5 g cm^{-3}) for the HDDR sample and by also considering a linear relationship between density and remanence.

Results and discussion

The variation in remanence and intrinsic coercivity of the permanent magnets produced as a function of aluminium content is shown in Figure 1. The remanence and intrinsic coercivity of the Al-free bonded $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ HDDR magnet were 0.69±0.01 T and 1.06±0.02 T, respectively. The remanence increased from 0.69±0.01 to 0.74±0.01 T when 0.1 at.% Al was added to the magnet. Higher Al contents decreased this magnetic property, reaching a minimum of 0.67±0.01 T with 0.5 at.% Al. The remanence of the $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ magnet observed in the present work, is lower than that reported in Ref. [3], and this can be attributed to differences in alloy purity and preparation conditions. Aluminium additions of 0.1 at.% decreased somewhat the intrinsic coercivity of the HDDR magnets. A peak in $_{i}H_{c}$ (1.27±0.03 T) was observed for the Pr-based magnet containing 0.3 at.% Al, and this is higher than the initial value of intrinsic coercivity shown by the Al-free magnet (1.06±0.02 T). Thus, the addition of 0.3 at.% Al to the Pr-Fe-Co-B-Nb alloy brings about an effective improvement, i.e., inducement of some anisotropy in the HDDR bonded magnets with substantial increase in the intrinsic coercivity. Higher Al contents decreased the intrinsic coercivity, reaching a minimum of 0.70±0.01 T with 1.0 at.% Al. The variation in remanence and intrinsic coercivity of the permanent magnets as a function of copper content is shown in Figure 2. Again, the remanence and intrinsic coercivity of the Al-free bonded $Pr_{14}Fe_{63.9-x}Co_{16}B_6Nb_{0.1}$ HDDR magnet, were taken as a reference. In the presence of only 0.1 at.% Cu, the remanence decreased from 0.69±0.01 to 0.62±0.01 T. Higher Cu contents decreased even further this magnetic property, reaching a minimum of 0.47±0.01 T with 1.0 at.% Cu. Copper additions also decreased substantially the intrinsic coercivity of the HDDR bonded magnets. The intrinsic coercivity decreased to a minimum of 0.20±0.01 T with 1.0 at.% Cu. Under the present processing conditions copper is deleterious to the magnetic properties of praseodymium-based HDDR bonded magnets.

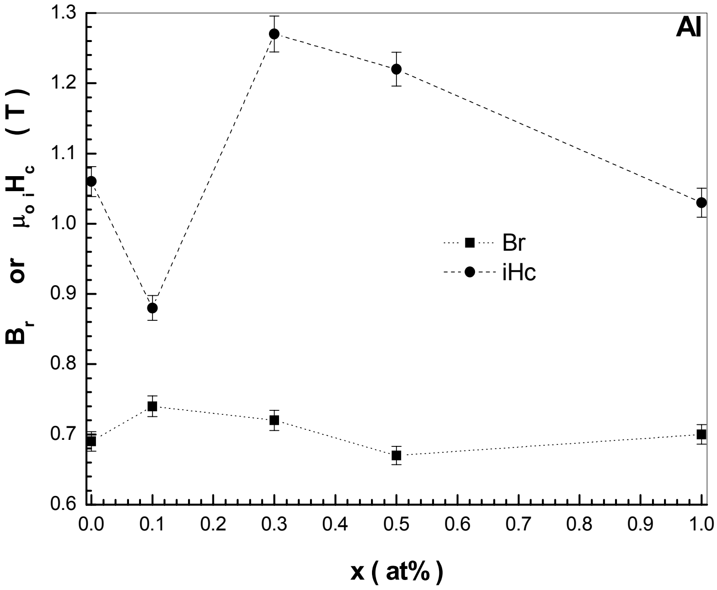

Fig. 1. Remanence and intrinsic coercivity versus aluminium content for bonded HDDR $Pr_{14}Fe_{63.9-x}Co_{16}B_6Nb_{0.1}Al_x$ magnets.

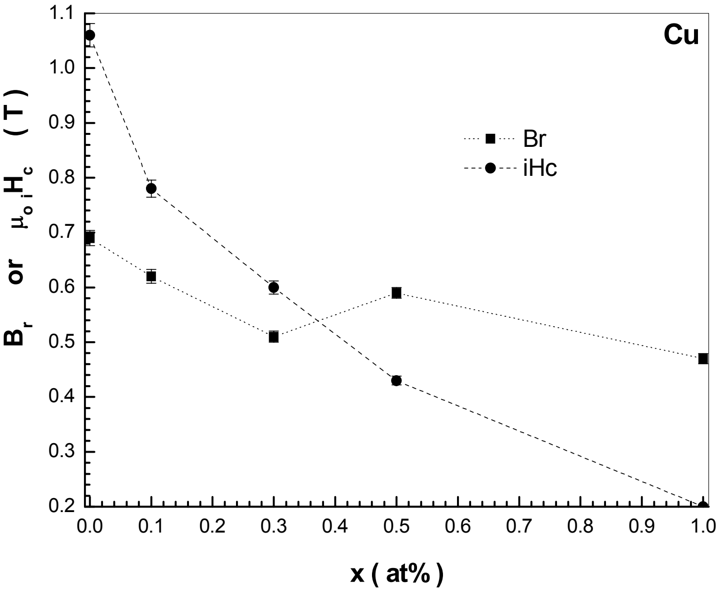

Fig. 2. Remanence and coercivity versus copper content for $Pr_{14}Fe_{63.9-x}Co_{16}B_6Nb_{0.1}Cu_x$ bonded magnets.

The variation in remanence and intrinsic coercivity of the permanent magnets produced from the annealed Pr-based alloys, as a function of phosphorous content is shown in Figure 3. The magnetic properties of the $Pr_{14}Fe_{63.9-x}Co_{16}B_6Nb_{0.1}$ magnet were also taken as a reference. In the presence of only 0.1 at.% P, the remanence increased from 0.69±0.01 to 0.77±0.01 T, which was the highest value obtained in the present work. Higher phosphorous contents slightly decreased this magnetic property, reaching a minimum of 0.72±0.01 T with 0.5 at.% P. Conversely, phosphorous additions of 0.1 and 0.3 at.% decreased somewhat the intrinsic coercivity of the HDDR magnets. A modest increase in ${}_iH_c$ was observed for the Pr-based magnet containing 0.5 at.% P, but this corresponds simply the recovery of the initial value of intrinsic coercivity shown by the P-free magnet. Thus, the addition of 0.1 at.% P to the Pr-Fe-Co-B-Nb alloy brings about an improvement in remanence, although at the expenses of the intrinsic coercivity. Nevertheless, it is necessary to emphasise that the amount of phosphorous, determined by analysis, in the $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}P_{0.1}$ alloy (given as weight %: 30.31Pr-54.75Fe-13.75Co-1.00B-0.14Nb-0.05P) is much lower than that specified in the formula. According to the supplier, part of the phosphorous added does not go into solution to any significant degree, forming an insoluble phosphate slag on the melt surface. Hence, the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.1}$ alloy contains some phosphorous, but less (~0.01wt%) than that suggested by the nominal composition (0.05wt%). Therefore, the probable substitution composition (atomic %) is $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.02}$. Reduced amount of phosphorous was also observed in the analyses of the alloys that should contain 0.3 and 0.5 at.% of this element.

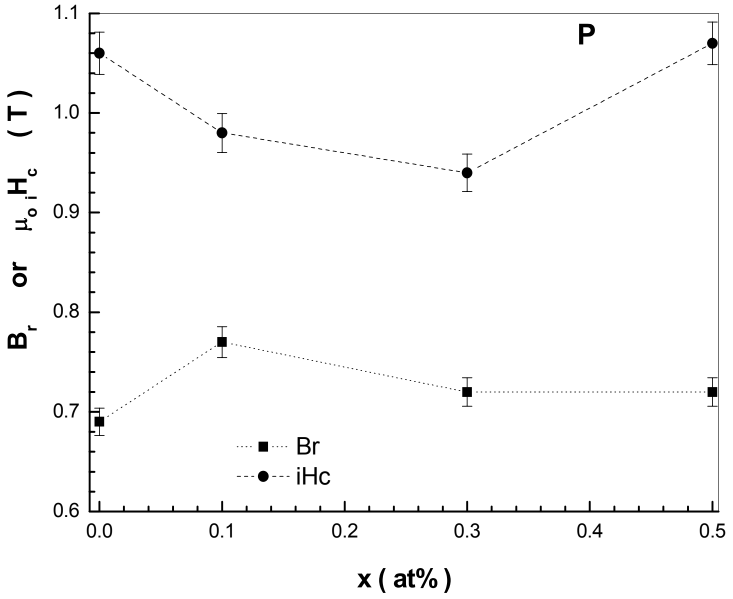

Fig. 3. Remanence and coercivity versus phosphorus content for $Pr_{14}Fe_{63.9-x}Co_{16}B_6Nb_{0.1}P_x$ bonded magnets.

The magnetic properties of the magnets produced using alloys with additions of Nb, Al, Si, Cu, Ga and Gd are shown in Table 2. Simultaneous additions of various elements resulted in an increase in remanence for the $Pr_{14}Fe_{63.6}Co_{16}B_6Nb_{0.1}Al_{0.1}$ magnet (N=2) and in coercivity for the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}Si_{0.1}Cu_{0.1}$ magnet (N=4). The magnetic properties of the Nb, Al, Si, Cu, Ga and Gd containing magnets with various contents of addition elements are shown in Table 3. The $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ HDDR bonded magnet still showed the best magnetic properties. A summary of the magnetic properties of all bonded magnets with the addition of only one extra element (N=2) is given in Table 4. Overall, concerning the magnetic properties, phosphorous and aluminium are the best addition elements to these praseodymium-based bonded magnets.

Table 2 Magnetic properties of $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}(M)_x$ HDDR bonded magnets (N= number of added elements to the $Pr_{14}Fe_{bal}Co_{16}B_6$ magnet).

Composition	N	B_r (T)	$\mu_o\,{}_iH_c$ (T)	$\mu_o\,{}_bH_c$ (T)	$(BH)_{max}$ (kJ/m^3)	SF (ratio)
$Pr_{14}Fe_{bal}Co_{16}B_6$	0	0.63±0.01	1.06±0.02	0.49±0.01	61.3±1.2	0.27±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$	1	0.69±0.01	1.06±0.02	0.51±0.01	79.3±1.6	0.37±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}$	2	0.74±0.01	0.88±0.02	0.51±0.01	78.0±1.6	0.34±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}Si_{0.1}$	3	0.69±0.01	0.95±0.02	0.48±0.01	65.1±1.3	0.34±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}Si_{0.1}Cu_{0.1}$	4	0.50±0.01	1.13 ±0.02	0.41±0.01	40.5±0.8	0.27±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}Si_{0.1}Cu_{0.1}Ga_{0.1}$	5	0.50±0.01	0.86 ±0.02	0.36±0.01	38.8±0.8	0.23±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}Si_{0.1}Cu_{0.1}Ga_{0.1}Gd_{0.1}$	6	0.60±0.01	0.78 ±0.02	0.39±0.01	46.6±0.9	0.23±0.01

Table 3 Magnetic properties of $Pr_{14}Fe_{63.9-5x}Co_{16}B_6Nb_{0.1}(AlSiCuGaGd)_x$ bonded magnets.

Composition	x	B_r (T)	$\mu_o\,{}_iH_c$ (T)	$\mu_o\,{}_bH_c$ (T)	$(BH)_{max}$ (kJ/m^3)	SF (ratio)
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$	0.00	0.69±0.01	1.06±0.02	0.51±0.01	79.3±1.6	0.37±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.01}Si_{0.01}Cu_{0.01}Ga_{0.01}Gd_{0.01}$	0.01	0.70±0.01	1.00 ±0.02	0.54±0.01	75.2±0.9	0.33±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}Si_{0.1}Cu_{0.1}Ga_{0.1}Gd_{0.1}$	0.10	0.60±0.01	0.78 ±0.02	0.39±0.01	46.6±0.9	0.23±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.3}Si_{0.3}Cu_{0.3}Ga_{0.3}Gd_{0.3}$	0.30	0.23±0.01	0.18 ±0.02	0.11±0.01	4.9±0.1	0.22±0.01

Table 4 Magnetic properties of $Pr_{14}Fe_{63.8}Co_{16}B_6Nb_{0.1}(M)_{0.1}$ HDDR bonded magnets.

Composition	N	B_r (T)	$\mu_o\,{}_iH_c$ (T)	$\mu_o\,{}_bH_c$ (T)	$(BH)_{max}$ (kJ/m^3)	SF (ratio)
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}$	2	0.74±0.01	0.88±0.02	0.51±0.01	78.0±1.6	0.34±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Si_{0.1}$	2	0.70±0.01	1.00±0.02	0.49±0.01	68.0±1.4	0.26±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Cu_{0.1}$	2	0.62±0.01	0.78±0.02	0.44±0.01	54.0±1.1	0.37±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Ga_{0.1}$	2	0.70±0.01	0.86±0.02	0.51±0.01	74.0±1.5	0.29±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Gd_{0.1}$	2	0.67±0.01	0.95±0.02	0.52±0.01	70.0±1.4	0.38±0.01
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}P_{0.1}$	2	0.77±0.02	0.98±0.02	0.56±0.01	85.9±1.7	0.37±0.01

Conclusions

As far as the magnetic properties are concerned, it has been shown that phosphorous and aluminium as addition elements improve the properties of praseodymium-based bonded HDDR magnets. The former induced considerable gain in anisotropy and the latter a substantial increase in intrinsic coercivity of these bonded magnets. In general, the addition of small contents was more beneficial to the HDDR bonded magnets. With the exception of squareness factor, the addition of copper proved detrimental to all magnetic properties of the Pr-based HDDR magnets. Simultaneous additions of various elements resulted in improved coercivity for the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}Al_{0.1}Si_{0.1}Cu_{0.1}$ bonded magnet (1.13±0.02 T) although the HDDR magnet containing 0.3 at.% Al ($Pr_{14}Fe_{63.6}Co_{16}B_6Nb_{0.1}Al_{0.3}$) showed an even higher intrinsic coercivity (1.27 ± 0.03 T).

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