THE EFFECT OF ALLOYNG ELEMENTS ON THE MICROSTRUCTURE AND PROPERTIES OF PrFeCoBNb SINTERED MAGNETS PRODUCED USING HIGH ENERGY MILLING

T. Mendes, S. C. Silva, E. P. Soares, E. A. Périgo, R. N. Faria, H. Takiishi
Av. Prof. Lineu Prestes 2242, 05508-000, São Paulo, Brazil,
teofilomendes@uol.com.br
Instituto de Pesquisas Energéticas e Nucleares

ABSTRACT

An evaluation of the effect of alloying elements on the microstructure and magnetic properties of $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}M_x$ *(M = Al, Cu, P, Si, Gd, Ga, Dy or Tb;* $0 \leq x \leq 0.5$*) sintered magnets has been carried out. A mixture of alloys and the high-energy milling technique have been used to prepare the magnets. The alloying elements have influenced the remanence, intrinsic coercivity and the squareness factor (SF). In general,* B_r *has been reduced somewhat for the magnets with alloying additions. On the other hand,* $\mu_{0i}H_c$ *and SF exhibited some improvements compared to the standard composition* $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ *magnet, particularly SF. The concentration of the alloying elements showed no influence on the density of the magnets, which ranged between 97% and 99% of the theoretical value. Comparisons between the squareness factors obtained using the* $J \times \mu_0 H$ *curve profile and the estimated using microstructural parameters have also been carried out.*

Keywords: High-energy milling, hydrogen decrepitation, PrFeB magnets, HD magnets.

INTRODUCTION

Substitutions of the neodymium for praseodymium may be applied with some advantages in sintered magnets, although various issues about their performance still must be addressed. $Pr_2Fe_{14}B$ has somewhat smaller magnetization, but the anisotropy field is 18% higher than $Nd_2Fe_{14}B$. Substitution of the neodymium for praseodymium avoids spin reorientation at low temperatures(1). Although Nd is more abundant than Pr, nowadays, praseodymium is cheaper due demand(2, 3).

Applications with permanent sintered (Nd-Pr)FeB magnets in high efficient motors require high temperature stability. In order to enhance Curie temperature (T_c), intrinsic coercivity ($\mu_{0i}H_c$), remanence (B_r) and temperature coefficients (α, β), additions is an effective approach(4). Chemical additions on the magnetic alloys selectively improve some properties but inevitably affect others. For example, partial substitution of Fe by Co increases Curie temperature but diminishes the coercivity. Additions of optimal combination of elements such as Al, Cu, Ga and Nb in sintered NdFeB magnets may be effective to change the microstructure and therefore the spontaneous polarization, squareness factor and anisotropy field. Al, Cu and Ga may form intergranular phases that modify neighbor hard magnetic grains(5). The better separation (decoupling) of the grains by secondary nonmagnetic phase leads to the enhancement of the coercivity(6) and can affect the corrosion resistance. NdFeB magnets containing small additions of cobalt and aluminum were found to exhibit excellent corrosion resistance attributed to the presence of Nd_3Co at the grain boundaries(7). Additions of P element has also been found to give a significant improve in corrosion resistance(8). Dy and Tb increase the anisotropy and thus the $\mu_{0i}H_c$ but decrease the remanence and the energy product(9).

In this work an evaluation of the magnetic and microstructure properties of HD sintered magnets prepared with $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}M_x$ (M = Al, Cu, P, Si, Gd, Ga, Dy or Tb; $0 \leq x \leq 0.5$) alloys and high energy planetary ball milled. The properties of the magnets were compared with obtained by standard composition $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$.

EXPERIMENTAL

Sintered permanent magnets were prepared of according to Faria et al[10] using a commercial alloy of composition $Pr_{16}Fe_{76}B_8$ (in the as-cast condition) which was blended with $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}M_x$ alloys (annealed at 1070 ^{0}C for 20 h), where M= Al, Cu, P, Si, Gd, Ga, Dy or Tb and x= 0.1, 0.3, 0.5 and 1.0 wt %. Sintered magnets were prepared by hydrogen decrepitation process (HD) by mixing the alloys in equal proportions (50 wt %). The HD material was planetary ball milled for 90 min. The fine hydride powder was aligned by pulsing three times to a 6 T magnetic field, pressed isostatically at a pressure of 200 MPa and the vacuum sintered for 1h at 1050^{o}C, followed by cooling on the furnace. Magnetic measurements of the sintered magnets were performed in a permeameter after saturation in a pulsed field of 6 T. The squareness factor was determined from the demagnetization curve ($SF=H_k/{}_iH_c$). Magnet densities were measured using a liquid displacement system. SEM backscattered electron micrographs to evaluate the microstructure the samples were polished an etched with aqua-regia. The micrographs were processed by a software image analyzer that produced data with important features about the elements additions influence. The mean grain size ($\bar{x}_{GS}$), elongation ($\bar{x}_E$), roundness ($\bar{x}_R$) and their respective deviation were been used to calculate the squareness factors based on microstructure parameters [11] defined by:

$$sf = 1 - \left[\frac{\sigma_{GS}}{\bar{x}_{GS}} \left(\frac{\sigma_E}{\bar{x}_E} + \frac{\sigma_R}{\bar{x}_R} \right) \right] \quad \text{(A)}$$

The homogeneity estimation of sintered magnets can be divided in two groups[11]: (i) size homogeneity, given by the mean grain size and standard deviation and, (ii) shape homogeneity, given by the grain roundness and elongation with their respective standard deviations.

RESULTS AND DISCUSSION

Magnetic properties

Remanence, intrinsic coercivity, energy product, squareness factor and density of the sintered magnets produced by the HD process and the blending method are shown in Table 1. It can be observed that the best $\mu_{0i}H_c$, compared to standard magnet $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$, was found to Ga addition (0.15 and 0.25 at. %). The intrinsic coercivity of sintered magnets is highly dependent of the microstructure and Ga or Al induce an effective enhancement in this magnetic property. This has been attributed to the better distribution of the Nd-rich intergranular phase due the solubility of the additive element in this phase(5). However, in the majority of the samples investigated in this work, a diminution of the intrinsic coercivity was observed. This can be attributed to the high amount of cobalt in the alloys compared to additive content. It has been reported that most additives have the undesirable effect of decreasing the magnetization of the main phase and, hence, the remanence(7). Most of the remanence values observed in this study are similar to that of the standard magnet. This can be attributed to the small amount of the additives elements. For particular element content, the squareness factor was improved with Gd, Ga and P. Further work is being carried out to clarify these microstructural features using transmission microscopy.

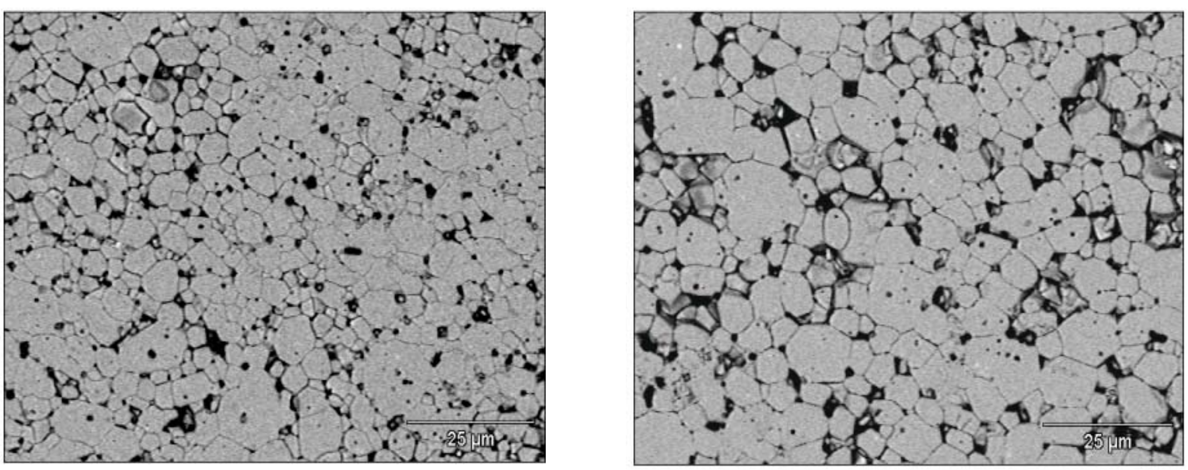
The values of remanence and maximum energy product given in Table 1 are in agreement to this correlation for the present HD sintered Pr-Fe-Co-B-Nb-M permanent magnets.

Table 1- Remanence, intrinsic coercivity, maximum energy product, squareness factor and density for the $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}M_x$ sintered magnets (M = Al, Si, P, Cu, Ga, Gd, Tb and Dy; x= 0.05; 0.15; 0.25 and 0.50).

M_x	B_r (mT) (± 2%)	$\mu_{0i}H_c$ (mT) (± 2%)	$BH_{(max)}$ (kJm^{-3}) (± 2%)	SF (± 2%)	ρ (g/cm^3) (± 0.5%)
Standard	1150	1000	247	0,84	7,41
$Al_{0,05}$	1120	910	230	0,78	7,48
$Al_{0,15}$	1080	950	210	0,71	7,43
$Al_{0,25}$	1140	970	242	0,80	7,43
$Al_{0,50}$	1130	940	238	0,83	7,43
$Si_{0,05}$	1120	800	230	0,85	7,55
$Si_{0,15}$	1100	850	218	0,81	7,53
$Si_{0,25}$	1140	1000	242	0,86	7,41
$P_{0,05}$	1080	900	214	0,81	7,38
$P_{0,15}$	1140	720	242	0,85	7,39
$P_{0,25}$	1170	880	254	0,89	7,48
$Cu_{0,05}$	1070	1040	215	0,77	7,47
$Cu_{0,15}$	1140	970	240	0,81	7,42
$Cu_{0,25}$	1060	920	202	0,67	7,43
$Cu_{0,50}$	1080	940	224	0,79	7,40
$Ga_{0,05}$	1090	1000	223	0,79	7,41
$Ga_{0,15}$	1150	1050	246	0,86	7,38
$Ga_{0,25}$	1060	1100	208	0,77	7,42
$Gd_{0,05}$	1050	850	216	0,87	7,46
$Gd_{0,15}$	1050	790	208	0,86	7,44
$Gd_{0,25}$	1120	690	225	0,86	7,48
$Tb_{0,15}$	1090	920	215	0,86	7,48
$Dy_{0,15}$	1050	910	207	0,82	7,48

Microstructural studies

Table 2 gives the mean grain size, elongation, roundness, and respective deviations used to analyze the homogeneity of the $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}M_x$ HD sintered magnets. In general, good agreement has been found between the squareness determined from the demagnetization curve (SF) and those determined from the microstructural analyses (sf). Figure 1a and b show the microstructures of the standard $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ HD magnet and the sintered $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}Ga_{0.25}$ magnet, respectively. Figure 2 shows the mean grain size distribution for these magnets. The grain size distributions follow a normal logarithmic distribution with a positive skew, i.e. there are smaller grains than large ones[12]. Demagnetization curves based on inhomogeneous nucleation mechanism for sintered Nd-Fe-B magnets assume that the reverse domains are formed at the surfaces of the grain where the anisotropy is reduced[12]. The intrinsic coercivity is a logarithmic function of the average number of surface defects per grain and, hence, on the average grain size[13]. This is in agreement with the present observations for the Pr-based sintered magnets with and without addition.



(a) (b)

Figure 1 – Microstructure of the sintered HD $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ (a) and $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}Ga_{0.25}$ (b) magnets (etched surface; magnification: 1000 X).

Table 2 -Mean grain size, elongation, roundness, microstructure factor (sf) and squareness factor (SF) for the sintered Pr-Fe-Co-B-Nb-M permanent magnets.

M_x	$X_{GS}\pm\sigma_{GS}$ (µm)	$X_E\pm\sigma_E$ no unit	$X_R\pm\sigma_R$ no unit	sf	SF (± 2%)
Standard	4,61 ±1,70	1,51 ±0,39	0,57 ±0,13	0,82	0,84
$Al_{0,05}$	5,52 ±1,94	1,46±0,60	0,70 ±0,13	0,86	0,78
$Al_{0,15}$	5,80 ±2,61	1,44 ±0,73	0,68 ±0,15	0,67	0,71
$Al_{0,25}$	5,49 ±2,56	1,47 ±0,47	0,69 ±0,18	0,89	0,80
$Al_{0,50}$	5,88 ±2,41	1,46 ±0,59	0,67 ±0,08	0,78	0,83
$Si_{0,05}$	4,52 ±1,80	1,55 ±0,43	0,67 ±0,18	0,78	0,85
$Si_{0,15}$	4,65 ±1,90	1,48 ±0,36	0,68 ±0,17	0,79	0,81
$Si_{0,25}$	4,54 ±1,89	1,44 ±0,71	0,62 ±0,11	0,83	0,86
$P_{0,05}$	5,80 ±2,76	1,45 ±0,32	0,67 ±0,15	0,78	0,81
$P_{0,15}$	4,73 ±1,93	1,43 ±0,28	0,68 ±0,15	0,82	0,85
$P_{0,25}$	5,65 ±2,07	1,41 ±0,25	0,69 ±0,08	0,89	0,89
$Cu_{0,05}$	5,78 ±2,93	1,38 ±0,36	0,71 ±0,17	0,74	0,77
$Cu_{0,15}$	6,11±2,90	1,47 ±0,51	0,65 ±0,09	0,76	0,81
$Cu_{0,25}$	5,22 ±2,31	1,44 ±0,29	0,69 ±0,20	0,77	0,67
$Cu_{0,50}$	5,57 ±2,47	1,47 ±0,33	0,68 ±0,19	0,77	0,79
$Ga_{0,05}$	6,43 ±2,76	1,39±0,28	0,68 ±0,08	0,85	0,79
$Ga_{0,15}$	6,08 ±2,74	1,40 ±0,31	0,67±0,11	0,82	0,86
$Ga_{0,25}$	5,42 ±2,37	1,48 ±0,46	0,66 ±0,09	0,79	0,77
$Gd_{0,05}$	5,30±1,85	1,46 ±0,34	0,56 ±0,11	0,84	0,87
$Gd_{0,15}$	5,29 ±1,94	1,45±0,33	0,66 ±0,09	0,87	0,86
$Gd_{0,25}$	5,61 ±2,25	1,49 ±0,33	0,63 ±0,14	0,81	0,86
$Tb_{0,15}$	5,69 ±2,40	1,43 ±0,33	0,68±0,14	0,80	0,86
$Dy_{0,15}$	5,49 ±2,16	1,47 ±0,32	0,67 ±0,09	0,85	0,82

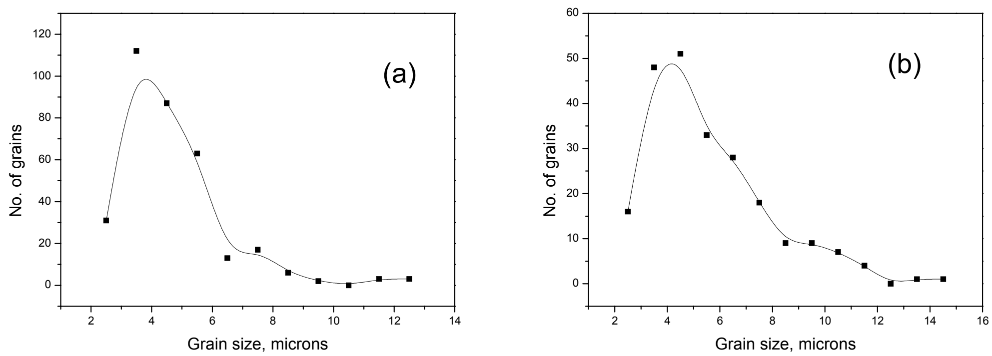


Figure 2 – Mean grain size distribution for the (a) $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ and (b) $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}Ga_{0.25}$ HD sintered magnets.

CONCLUSIONS

Gallium addition can be effective to enhance the intrinsic coercivity of the $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}M_x$ HD sintered permanent magnets at the expense of the other magnetic properties. Phosphorus and gadolinium additions improve the squareness factor and, as predict in a particular correlation, the maximum energy product. The squareness factor determined form the demagnetization curves showed a reasonable agreement with the factor based microstructural parameters. Good homogeneity factor has been found for the addition of aluminum and phosphorus on the $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ standard magnet. It has also been shown that the grain size distributions of the standard and $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}Ga_{0.25}$ magnets follow a logarithmic distribution.

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