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THE EFFECT OF Cu, P, Ga and Gd ON MICROSTRUCTURE AND MAGNETIC PROPERTIES IN THE PrFeCoBNb HD SINTERED MAGNETS

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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 = Cu, P, Gd and Ga; $0 \leq x \leq 0.25$) 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 particularly the squareness factor (SF). Phosphorus addition improved $(BH)_{max}$ (254 kJm^{-3}) and SF around 10% (0.89). The same improvement addition on intrinsic coercivity was observed with Gallium (1100mT) compared to the standard composition $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ (1000mT) magnet. Comparisons between the squareness factors obtained using the $J \times \mu_0 H$ curve profile (SF), the estimated (sf) using microstructural parameters and Sf using a $(BH)_{max}$ and B_r correlation have also been carried out.

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. 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]. Processing conditions can also change the squareness factor and consequently the $(BH)_{max}$[14]. In the present study different concentration of elemental addition were utilized to produce PrFeCoBNb HD sintered magnets and were been analyzed to evaluate the influence on the microstructure and magnetic properties.

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 ^0C for 20 h), where M= Cu, P, Gd, Ga and x= 0.1, 0.3, and 0.5 at. %. Sintered magnets were prepared using the hydrogen decrepitation process (HD) by mixing the alloys in equal proportions. The HD material was planetary ball milled for 90 min. The fine hydride powder was aligned by pulsing three times in 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 were used to evaluate the microstructure of the magnets and the polished samples were etched with aqua-regia. The micrographs were analyzed using a software image analyzer. 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 defined by[11]:

$$sf = 1 - \left[\frac{\sigma_{GS}}{\overline{x}_{GS}} \left(\frac{\sigma_E}{\overline{x}_E} + \frac{\sigma_R}{\overline{x}_R} \right) \right]. \qquad (1)$$

The homogeneity estimation of sintered magnets can be divided in two groups: (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[11].
For comparison, the squareness factor was also calculated employing $(BH)_{max}$ and B_r according to relation[15]:

$$Sf = \frac{4\mu_0 (BH)_{max}}{B_r^{\ 2}} \qquad (2)$$

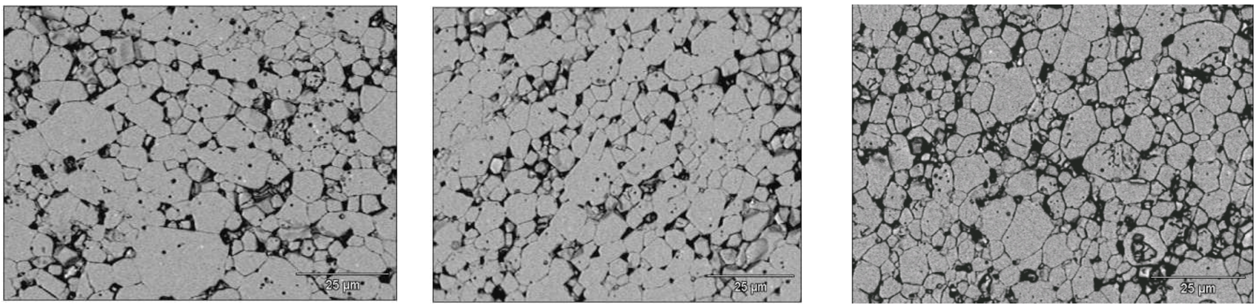
Results and discussion

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 (0.25 at. %) that improved around 10% in this properties. The intrinsic coercivity of sintered magnets is highly dependent of the microstructure and Ga or Al induced 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 could 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. In this work P, Ga and Ga improved the squareness factor. This is probably due an optimal combination with Co as the main and P, Ga and Gd as the minor additions[16]. These elements probably improved wettability of the rich phase enhancing the homogeneity of the microstructure (eq. 1). The values of remanence and maximum energy product given in Table1 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 = P, Cu, Ga and Gd, x= 0.05; 0.15 and 0.25).

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
$P_{0.05}$	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
$Ga_{0.05}$	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

Figs. 1 (a, b, c) shown micrographs of the sintered magnets $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ with Ga, P and Gd (0.25 at. %) additions, respectively. The mean grain size presented from these magnets presented values next to 5.6 µm (listed on Table 2). The evaluation of the micrographs (a), (b) and (c) showed good grain size homogeneity and confirm that this plays a more important role in the SF than does grain shape homogeneity[11]. Higher intrinsic coercivity on sample (a) can be attributed probably to the better solubility of the additive element Ga in the Pr-rich phase. Further studies with SEM (no chemical etched) and transmission microscopy must be carried out to confirm these results.



a) b) c)

Figs. 1 - Microstructure of the sintered magnets $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ with (a) $Ga_{0.25}$, (b) $P_{0.25}$ and (c) $Gd_{0.25}$ additions. The $\mu_{0i}H_c$ values were: a) 1100, b) 880 and c) 690 mT.

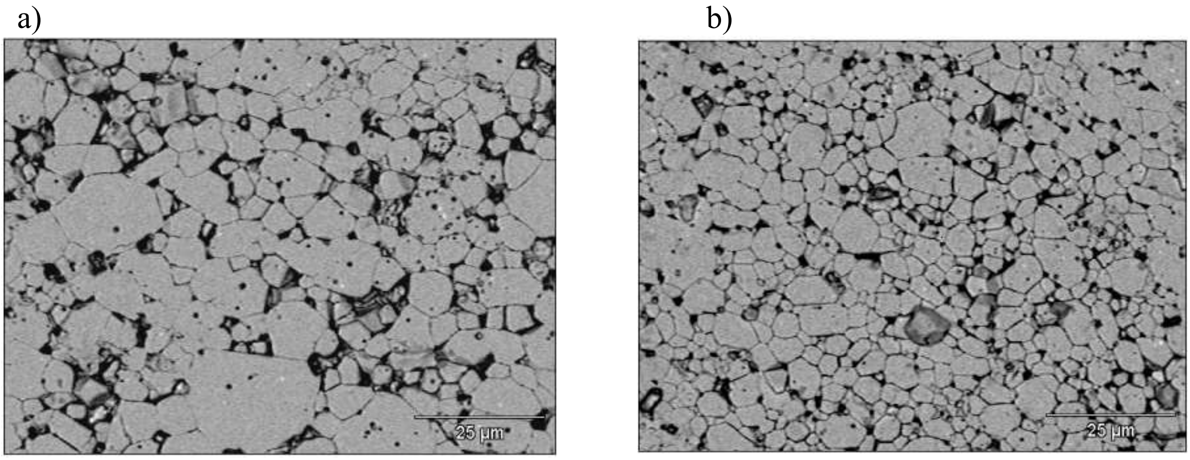


Fig. 2- Microstructure of the sintered HD $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ (a) a $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}Ga_{0.25}$ (b) magnets (etched surface; magnification: 1000X).

Microstructural studies. Fig. 2 (a,b) shown the microstructures of the standard $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ and $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}Ga_{0.25}$ HD sintered magnets, respectively. Fig.3 shown 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]. 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 HD sintered magnets with Ga addition and the standard. It can be observed that Ga addition increased about 15 % on the mean grain size compared with standard magnet.

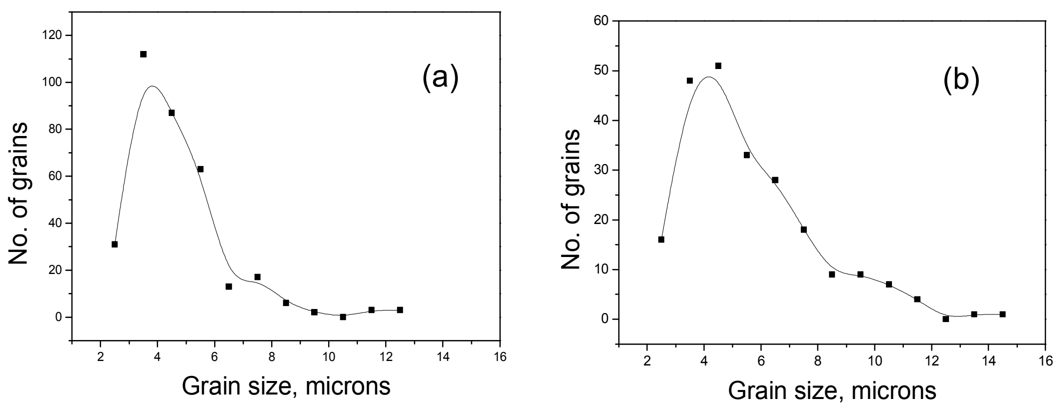


Fig. 3- Grain size distribution for the (a) $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ and ($Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}Ga_{0.25}$ HD sintered magnets.

Table 2 lists 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 varying atomic number (Z) of the addition elements. In general, these additions enlarged the mean grain size when compared to the standard magnet. Silicon addition showed no effect on the mean grain size probably despite poor solubility in the Pr rich phase.

Table 2 - Mean grain size, elongation, roundness and respective standard deviations for the sintered Pr-Fe-Co-B-Nb-M permanent magnets varying atomic number (Z).

M_x	Z	$X_{GS}\pm\sigma_{GS}$ (µm)	$X_E\pm\sigma_E$ (no unit)	$X_R\pm\sigma_R$ (no unit)
Standard		4.61 ±1,70	1.51 ±0,39	0.57 ±0,13
$P_{0.05}$	15	5.80 ±2,76	1.45 ±0,32	0.67 ±0,15
$P_{0.15}$		4.73 ±1,93	1.43 ±0,28	0.68 ±0,15
$P_{0.25}$		5.65 ±2,07	1.41 ±0,25	0.69 ±0,08
$Cu_{0.05}$	29	5.78 ±2,93	1.38 ±0,36	0.71 ±0,17
$Cu_{0.15}$		6.11±2,90	1.47 ±0,51	0.65 ±0,09
$Cu_{0.25}$		5.22 ±2,31	1.44 ±0,29	0.69 ±0,20
$Ga_{0.05}$	31	6.43 ±2,76	1.39±0,28	0.68 ±0,08
$Ga_{0.15}$		6.08 ±2,74	1.40 ±0,31	0.67±0,11
$Ga_{0.25}$		5.42 ±2,37	1.48 ±0,46	0.66 ±0,09
$Gd_{0.05}$	64	5.30±1,85	1.46 ±0,34	0.56 ±0,11
$Gd_{0,15}$		5.29 ±1,94	1.45±0,33	0.66 ±0,09
$Gd_{0.25}$		5.61 ±2,25	1.49 ±0,33	0.63 ±0,14

Squareness factor evaluation. Figure 4 shows the variation on the various squareness factors as a function of the atomic number (Z) of the addition element. A similar behavior can be noted to SF and sf factor. Sf calculated with relation (2) showed superior values for all samples and can be considered appropriated for special profile curves (Sf near 1.0). In general, good agreement has been found between the squareness factor determined from the demagnetization curve (SF) and those determined from the microstructural analyses (sf).

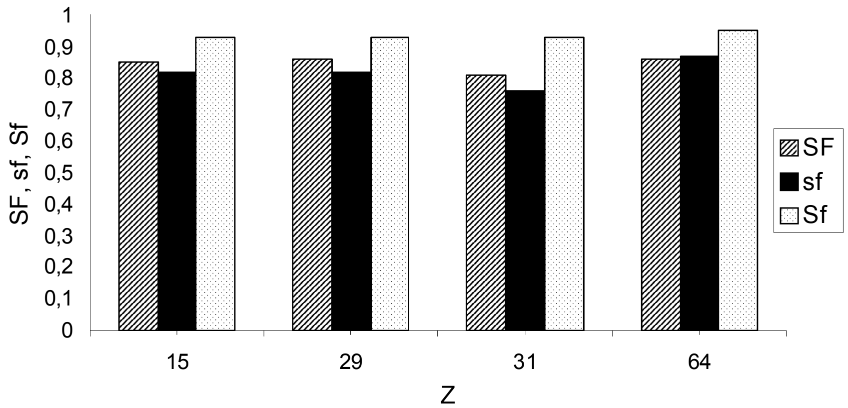


Figure 4 –SF, sf and Sf variation of the sintered magnets plotted against the atomic number (Z) of the addition elements on the standard $Pr_{15}Fe_{bal}Co_8B_7Nb_{0.05}$ alloy.

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 from the demagnetization curves showed a reasonable agreement with the factor based on microstructural parameters. Good homogeneity factor has been found for the addition of 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.

Acknowledgements

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