Materials Science Forum
ISSN: 1662-9752, Vol. 930, pp 440-444
doi:10.4028/www.scientific.net/MSF.930.440
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Submitted: 2018-01-22
Accepted: 2018-01-29
Online: 2018-09-14

Influence of Alloying Elements Zr, Nb and Mo on the Microstructure and Magnetic Properties of Sintered Pr-Fe-Co-B Based Permanent Magnets

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Keywords: Rare-earth permanent magnets; Pr-Fe-Co-B based magnets; hydrogen decrepitation.

Abstract. The addition of alloying elements on rare-earth permanent magnets is one of the methods used to improve the magnetic properties. This present work evaluates the influence of alloying elements such as Zr, Nb and Mo on the microstructure and magnetic properties of sintered Pr-FeCo-B based permanent magnets. The permanent magnets were produced by the conventional powder metallurgy route using powder obtained by hydrogen-decrepitation (HD) method from as cast alloys. In order to produce the magnet $Pr_{16}Fe_{66,9}Co_{10,7}B_{5,7}Cu_{0,7}$ without alloying elements the mixture of alloys method was employed, mixing two compositions: $Pr_{20}Fe_{73}B_5Cu_2$ (33% w.t) and $Pr_{14}Fe_{64}Co_{16}B_6$ (67% w.t). With the purpose of evaluating the influence of the alloying elements, the $Pr_{14}Fe_{64}Co_{16}B_6X_{0,1}$ (where X= Zr, Nb or Mo) (67% w.t) alloy was employed. The characterization of the alloys and the magnets was carried out using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS) and the magnetic properties were measured using a permeameter. The magnet without any additions presented the highest intrinsic coercivity ($\mu_{0i}H_c$ = 748 KA.m-1) while the magnet with Nb addition presented higher remanence (Br = 1,04 T). The magnet with Zr addition presented the highest maximum energy product ($BH_{máx}$ = 144 $KJ.m^{-3}$), and the magnet with Mo addition showed the highest squareness factor (SF = 0,73).

Introduction

Since the 80's, the evolution in development and research of the permanent magnets boosted the development of many technological fields such as electrical, electronic and telecomunication engineering [1].

One of the most promising applications of the permanent magnets is in the generation of green energy, such as, in the production of electric and hybrid vehicles and at wind generators. The increasing demand for clean energy, allied to Chinese restrictions to rare earth exportation and high prices, boosted the research in this class of materials [2, 3, 4].

The powder metallurgy route is the main production route of the rare-earth permanent magnets, and the hydrogen-decrepitation (HD) method is extremely important in the production of the powders, because besides the elimination of the crushing ingots stage, it also reduces grinding time [5].

Alloying elements additions aims the improvement of the magnetic properties and allows the study of better chemical composition and the effects of each alloy element on the microstructure [6].

Experimental

The compositions $Pr_{20}Fe_{73}B_5Cu_2$ (33% wt) and $Pr_{14}Fe_{64}Co_{16}B_6$ (67% wt) were used to produce the sintered magnets with final composition $Pr_{16}Fe_{66.9}Co_{10.7}B_{5.7}Cu_{0.7}$. In order to evaluate the influence of the alloying elements additions, the $Pr_{14}Fe_{64}Co_{16}B_6X_{0.1}$ (X= Zr, Nb or Mo) (67%wt) alloy was used. Both the $Pr_{14}Fe_{64}Co_{16}B_6$ and $Pr_{14}Fe_{bal}Co_{16}B_6X_{0.1}$ alloys were previously heat treated at 1373 K for 20 h in a furnace with a vacuum system in the order of 10^{-5} mBar, to ensure the elimination of the Fe-rich phase. The $Pr_{20}Fe_{73}B_5Cu_2$ alloy was used without heat treatment. After the heat treatment step, pieces of the ingots were placed in a crucible, according to the stoichiometric ratio of each alloy. Hydrogen (H_2) was introduced with pressure of 2,000 mBar, which was absorbed by the alloy, forming hydrides and making the material friable, facilitating the obtainment of fine powders. The resultant powders from HD process were milled in a planetary mill for 90 minutes at 200 rpm speed with cyclohexane as milling medium. The milling vessel was then conected to a drying and transfering system, where the powder was transfered to a rubber mold [7], which was aligned in a 6 T magnetic field. Thereafter, the powder was isostatically pressed at 200 MPa. The sample was placed in a stainless steel tube with a vacuum system in the order 10^{-5} mBar. The matrix phase ($Pr_2Fe_{14}B$) dehydrogenation was conducted at a 5 K/min rate up to 573 K, and kept in that temperature for 20 minutes, and the dehydrogenation of the Pr-rich phase was also conducted at a 5 K/min rate up to 973 K, and kept in that temperature for 20 minutes for pressure stabilization. Finally, the temperature was increased up to 1333 K at 7K/min and remained in this temperature for 60 minutes for sintering.

The alloys and the produced magnets were characterized by scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDXS) and the magnetic properties were obtained using a permeameter.

Result and Discussion

The microstructures of the produced magnets are shown in Fig.1a-d. Fig.1a shows the magnet $Pr_{16}Fe_{66.9}Co_{10.7}B_{5.7}Cu_{0.7}$ without additions. Fig.1 b-d presents the magnets with alloying elements additions with the compositions $Pr_{16}Fe_{66.9}Co_{10.7}B_{5.7}Cu_{0.7}Zr_{0.07}$, $Pr_{16}Fe_{66.9}Co_{10.7}B_{5.7}Cu_{0.7}Nb_{0.07}$ e $Pr_{16}Fe_{66.9}Co_{10.7}B_{5.7}Cu_{0.7}Mo_{0.07}$, respectively.

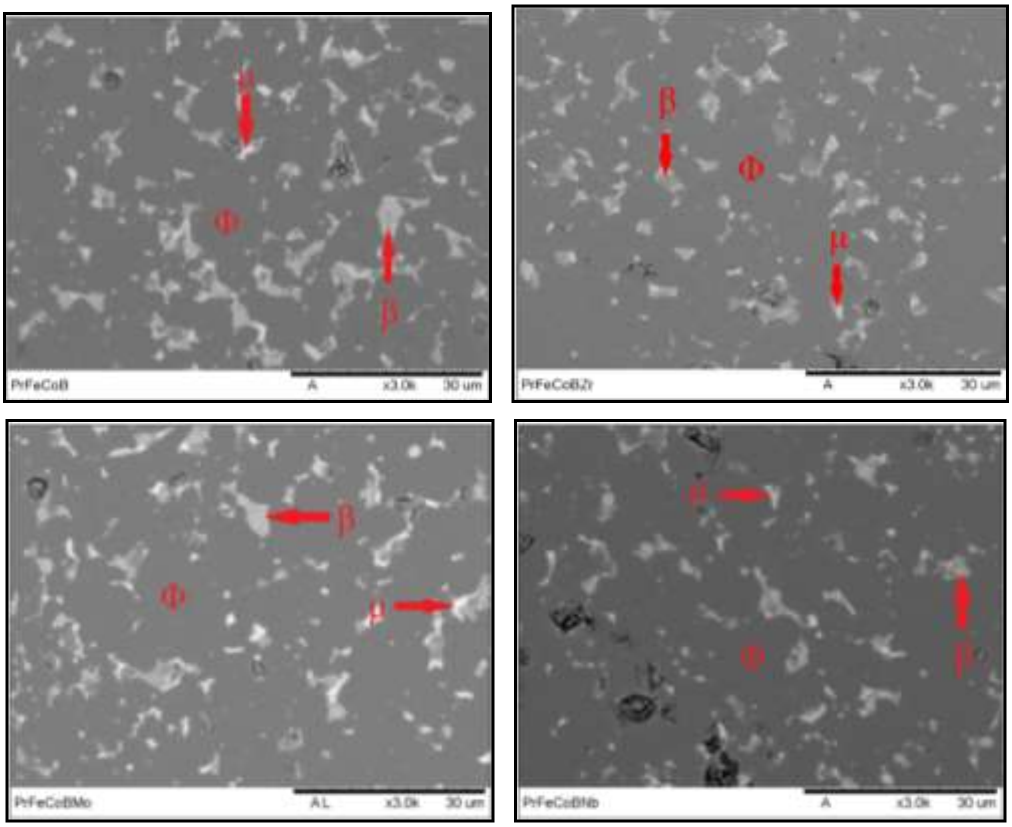
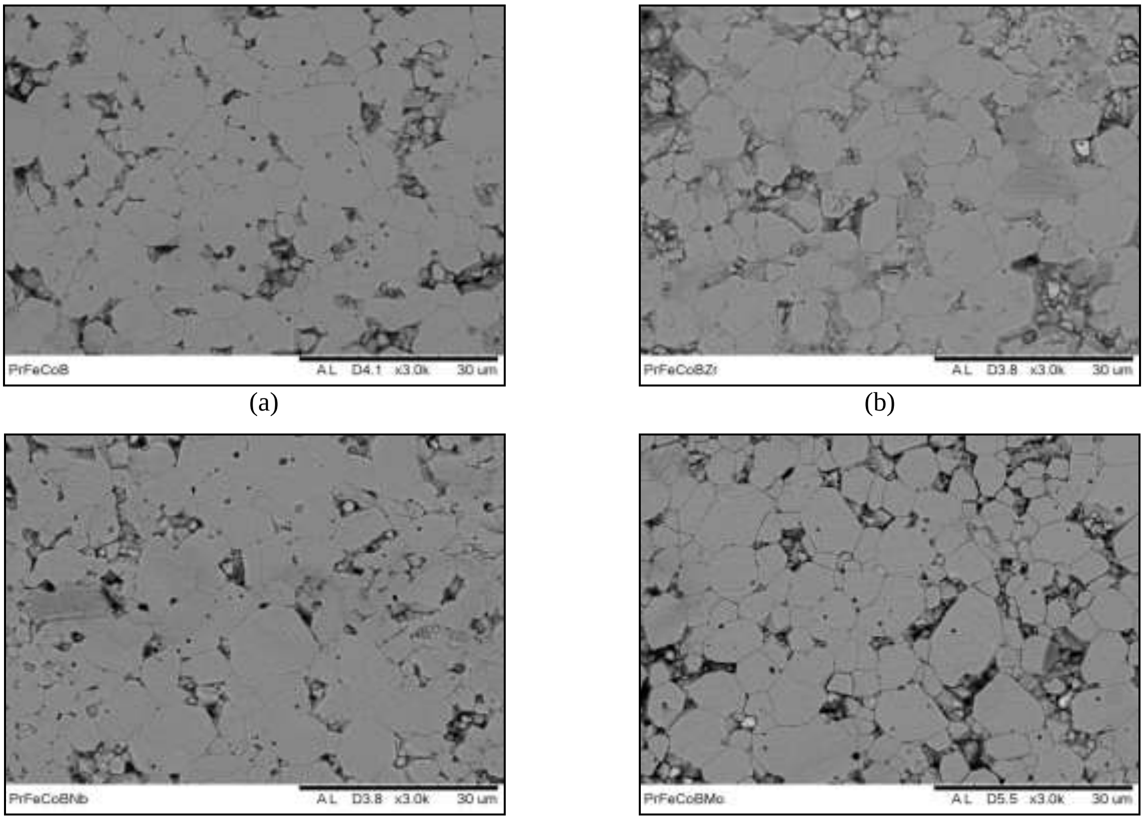


Fig. 1. SEM images of the magnets: (a) without additives, (b) with Zr addition, (c) with Nb addition and (d) with Mo addition.

All the images has been shown the typical microstructure of RE-Fe-B, which the three main phases are: matrix ($Pr_2Fe_{14}B$ – Φ), Pr-rich phase ($Pr_3(FeCo)$ – μ) and Laves phase ($Pr(FeCo)_2$ – β). No phase changes due the additions have been observed in the micrographs and the EDS analyses. These alloying elements have been cited in the literature as acting in the grain boundaries refining the microstructure [6]. In order to reveal the grain boundaries, the samples were etched with Marble solution, as shown in Fig.2a-d.

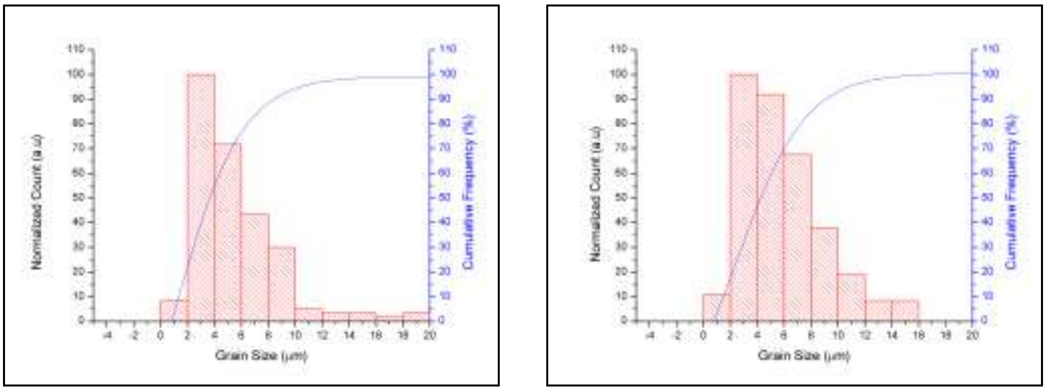


(a) (b)

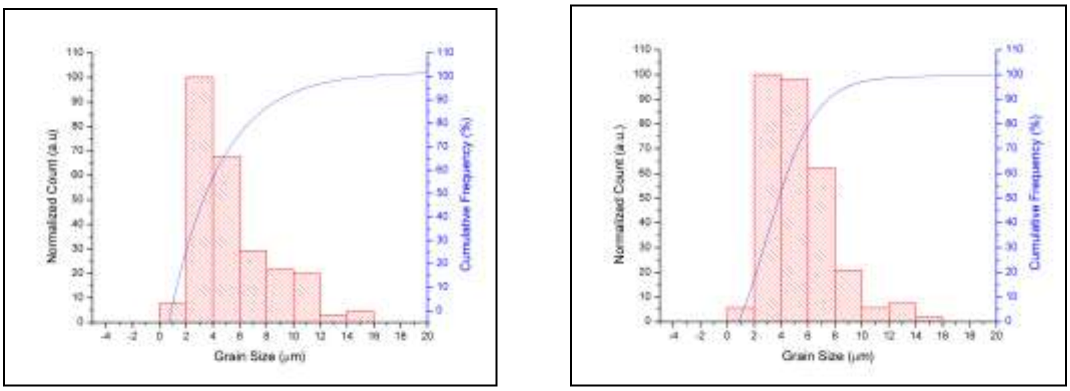
(c) (d)

Fig. 2. SEM images of the magnets: (a) without addition, (b) with Zr addition, (c) with Nb addition and (d) with Mo addition. Surface treatment: Marble.

Zirconium may have contributed to produce a microstructure with rounder grains, and molybdenum may have produced less heteregeneous grain size distribution. Although, it has been observed that all microstructures show similar mean grain size, format and distribution, indicating that the additions did not promote drastic changes in all microstructures since the processing was the same for all samples. Grain size distribution analysis was carried out using the image analyzer ImageJ. Fig.3a-d presents the grain size distribution histograms and Table 1 summarizes the obtained results.



(a) (b)



(c) (d)

Fig. 3. Grain size distribution of the magnets: (a) without addition; (b) with Zr; (c) with Nb and (d) with Mo.

Table 1. Mean grain sizes and its standard deviations.

Added elements	without addition	Zr	Nb	Mo
Mean grain size (µm)	5.5	5.9	5.5	5.3
Standard deviation (µm)	3.2	3.1	3.0	2.5

The histograms have shown that the mean grain size for all samples are close to each other and its distribution is heterogeneous. However, the magnet with Mo addition has presented a slight improvement in grain size distribution. The Zr, Nb and Mo additions are known to act in the grain boundaries refining the microstructure; though in this present studies it has not been possible to identifytheir acting mechanisms. Even though, it has been observed that all additions promoted a microstructural refinement, because the sample without additions haves hown grains larger than 16 µm while the samples with additions have presented grains with maximum size under 16 µm.

Magnetic properties of the magnets produced have been obtained from the second quadrant of the hysteresis curve, as shown in Fig.4, and summarized in Table 2. The density values obtained by Archimedes' method have been compared to theoretical density (7.53 g.cm^{-3}) and are shown as well.

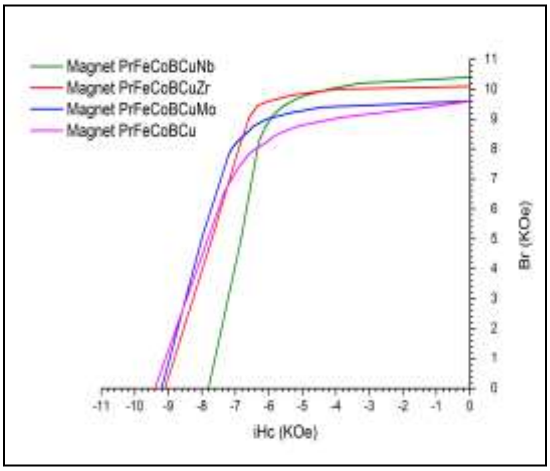


Fig. 4. Demagnetization curves.

Table 2. Magnetic properties and density of the magnets produced.

Composition	B_r (T)	$_iH_c$(KA.m^{-1})	$_bH_c$ (KA.m^{-1})	$(BH)_{max}$ (KJ.m^{-3})	Squareness fator (no unit)	Density (%)
PrFeCoBCu	0.96	748	557	134	0.57	93
PrFeCoBCuZr	1.01	724	565	144	0.70	96
PrFeCoBCuNb	1.04	620	517	138	0.72	96
PrFeCoBCuMo	0.96	732	581	141	0.73	97

The magnet without addition have presented the highest intrinsic coercivity (${}_iH_c$ = 748 KA.m^{-1}), while the magnet with Nb addition have presented the highest remanence (Br = 1.04 T). The magnet with Zr addition have presented the highest maximum energy product ($(BH)_{máx}$ = 144 KJ.m^{-3}) while the magnet with Mo addition have presented the highest squareness factor (SF = 0.73).

Conclusion

Many works show that the additions of alloying elements resulted in an increase of coercivity and squareness factor in expense of remanence [8]. In this present work, it has been observed that all addition of Zr, Nb and Mo led to an increase of the squareness factor in the order of 28% and a slight increase of remanence, but led to a decrease of intrinsic coercivity in the order of 17%. However, the densities have increased with all additives, as expected. The alloying elements addition improves some magnetic properties, but inevitably affects other magnetic properties, such as, partial substitution of Fe for Co, that increases the Curie temperature but diminishes the coercivity.

Acknowledgements

The authors acknowledge IPEN for the infrastructure, CNPq for the scholarship granted and FAPESP – process nº 2001/03961-4 and process nº 2015/26723-4, São Paulo Research Foundation.

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