

Microestrutural and Magnetic Properties Characterization of PrFeCoB-Based Alloys and Permanent HD Sintered Magnets

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Resumo

Os ímãs foram preparados via metalurgia do pó, a partir de pós obtidos pelo processo de Decrepitação por Hidrogênio (HD). As composições das ligas utilizadas foram: $\text{Pr}_{20}\text{Fe}_{\text{bal}}\text{B}_5\text{Cu}_2$ (33% em peso) e $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_x$ (onde $x = 0,3$ e $0,5$) (67% em peso). As ligas utilizadas e os ímãs produzidos foram caracterizados por Fluorescência de Raios-X (FRX), Microscopia Eletrônica de Varredura (MEV), Espectroscopia de Energia Dispersiva (EDS), Difração de Raios-X (DRX), e as propriedades magnéticas foram obtidas por meio de Permeâmetro. Os resultados mostraram que o ferro livre contido nas ligas é prejudicial às propriedades magnéticas dos ímãs, e que a otimização dessas propriedades, é devido à eliminação desse constituinte mediante a um tratamento térmico (1343K por 20 horas). Assim, os ímãs produzidos com as ligas tratadas termicamente apresentaram produto de energia máxima superior a 50% em relação aos ímãs produzidos com a liga não tratada. O ímã, produzido com a liga $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_{0,5}$ tratada termicamente, apresentou os melhores valores de remanência ($B_r = 1.03$ T), produto de energia máximo $((\text{BH})_{\text{máx}} = 201.6 \text{ KJ.m}^{-3})$ e coercividade intrínseca ($iH_c = 716.2 \text{ KA.m}^{-3}$).

Abstract

The magnets were produced by powder metallurgy route, using powders obtained by hydrogenation-decrepitation method (HD). The compositions of the alloys were: $\text{Pr}_{20}\text{Fe}_{\text{bal}}\text{B}_5\text{Cu}_2$ (33% wt.) and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_x$ (where $x = 0,3$ e $0,5$) (67% wt.). The characterization of the alloys and the magnets produced have been carried out using backscattered electron microscopy (BEM), energy-dispersive X ray spectroscopy (EDXS), X ray diffraction (XRD), X ray fluorescence (XRF) and magnetic properties have been measured using a permeameter. The results revealed that the Fe-rich phase is prejudicial to magnetic properties and the improvement of the properties is due to the elimination of the Fe-rich phase by heat treatment (1343K for 20 hours). Therefore, the magnets produced by heat treated alloys presented a maximum energy product 50% higher when compared with the magnets produced by as-cast alloys. The magnet produced by $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_{0,5}$ heat treated alloy presented the best values for remanence ($B_r = 1.03$ T), maximum energy product $((\text{BH})_{\text{máx}} = 201.6 \text{ KJ.m}^{-3})$ and intrinsic coercivity ($iH_c = 716.2 \text{ KA.m}^{-3}$).

Keywords (Palavras chaves): PrFeCoB magnets; Hydrogen decrepitation, Rare-earth permanent magnets

1. Introduction

Rare earth magnets have a relevant role in the electromagnetic devices industry, especially for the clean energy generation, such as that produced by wind generators and electric and hybrid vehicles [1,2].

An increase in the clean energy demand, besides Chinese restrictions to rare earth exportation and high prices, boosted research in this class of magnets [3,4,5].

The most used method to produce permanent magnets is the powder metallurgy. The decrepitation hydrogen process (HD) is highly relevant in the magnets production, because besides the elimination of the crushing ingots stage, it also reduces grinding time, easing studies of different compositions in laboratory scales [6,7].

2. Methodology

The compositions $\text{Pr}_{20}\text{Fe}_{\text{bal}}\text{B}_5\text{Cu}_2$ (33wt%) and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_x$ ($x = 0,3$ e $0,5$) (67wt%) were used to produce the sintered magnets. The $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_x$ alloy was previously heat treated at 1343K for 20h in a furnace with a vacuum system in the order of 10^{-5} mBar, to ensure the elimination of the phase rich in iron. The $\text{Pr}_{20}\text{Fe}_{\text{bal}}\text{B}_5\text{Cu}_2$ alloy was used without heat treatment.

After heat treatment, 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 200 mBar, which was absorbed by the alloy, forming hydrades and making the material friable, facilitating the obtainment of fine powders.

The HD resulting powder was ground in a high energy planetary mill for 90 minutes at a speed of 200 rpm amid cyclohexane. The grinding recipient was connected to a drying and transporting system, where the powder was transferred to a mold [8]. The mold containing the powder was submitted to a pulsed magnetic field of 6T to align the grains and optimize the magnets magnetic properties.

Thereafter, the powders were compacted in an isostatic press with pressure of 200MPa. The sample was placed in a stainless steel tube with a vacuum

system in order 10^{-5} mbar. The matrix phase ($\text{Pr}_2\text{Fe}_{14}\text{B}$) dehydrogenation was conducted at a 5 K/min rate up to 573K, and kept in that temperature for 20 minutes, and the dehydrogenation of the phase rich in praseodymium was also conducted at a 5 K/min rate up to 973K, and kept in that temperature for 20 minutes for pressure stabilization. Lastly, the temperature was increased up to 1333K at 7 K/min and remained in this temperature for 1 hour to sinter.

With the mixture of the alloys $\text{Pr}_{20}\text{Fe}_{\text{bal}}\text{B}_5\text{Cu}_2$ (33 wt%) and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_{0,3}$, (67 wt%), both without heat treatment, the magnet named "A1", with composition of $\text{Pr}_{16}\text{Fe}_{\text{bal}}\text{Co}_{11,07}\text{B}_{5,69}\text{Nb}_{0,07}\text{Cu}_{0,82}(\text{AlSiGaGd})_{0,21}$, was produced. To produce the magnet called "A2", with the same composition, the heat treated alloy $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_{0,3}$, (67 wt%) was used. Similarly, the magnet named "B1" with composition of $\text{Pr}_{16}\text{Fe}_{\text{bal}}\text{Co}_{11,07}\text{B}_{5,69}\text{Nb}_{0,07}\text{Cu}_{0,96}(\text{AlSiGaGd})_{0,35}$ was produced with the mixture of the alloys $\text{Pr}_{20}\text{Fe}_{\text{bal}}\text{B}_5\text{Cu}_2$ (33 wt%) and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_{0,5}$, (67 wt%), both without heat treatment. To produce the magnet named "B2", with the same composition, the heat treated alloy $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_{0,5}$, (67 wt%) was used.

The alloys used and magnets produced were characterized by X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Fluorescence Spectroscopy (EDS), X-ray diffraction (XRD), and the magnetic properties were obtained using a permeameter.

3. Results and Discussion

The micrographs show the presence of four phases in the as cast alloys, while in the heat treated alloys there is only three phases. Figures 1 and 2 present the micrographs of the alloy $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0,1}(\text{AlSiCuGaGd})_{0,3}$ before and after heat treatment, respectively.

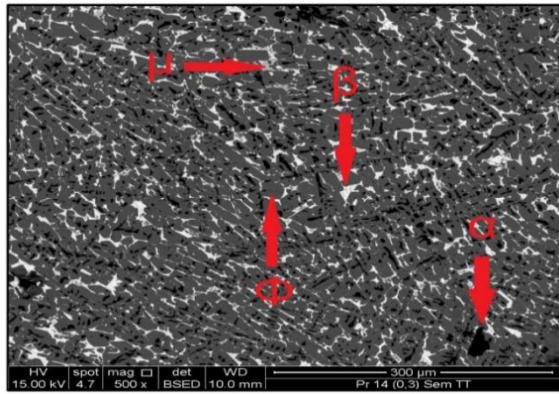


FIGURE 1: SEM micrograph of the alloy $Pr_{14}Fe_{60}Co_{16}B_6Nb_{0.1}(AlSiCuGaGd)_{0.3}$ as cast. The identified phases were: the matrix $Pr_2(FeCo)_{14}B$ (α), the phase rich in praseodymium $Pr_3(FeCo)$ (β), Laves phases $Pr(FeCo)_2$ (μ) and the phase rich in iron $FeCo$ (α).

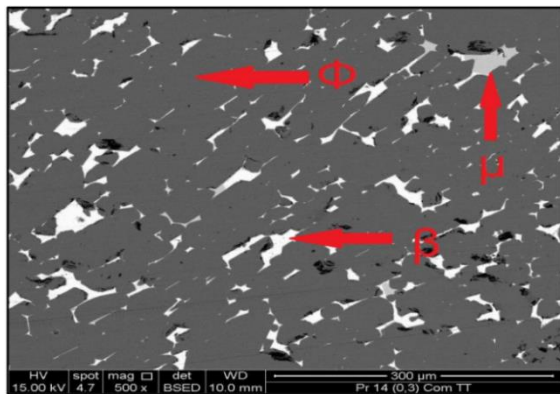


FIGURE 2: SEM micrograph of the alloy $Pr_{14}Fe_{60}Co_{16}B_6Nb_{0.1}(AlSiCuGaGd)_{0.3}$ after heat treatment. The identified phases were: the matrix $Pr_2(FeCo)_{14}B$ (α), the phase rich in praseodymium $Pr_3(FeCo)$ (β) and the Laves phases $Pr(FeCo)_2$ (μ).

X-ray diffraction analyses were performed to verify the phases present in the alloys, identified by EDS. The XRD patterns obtained for the alloy $Pr_{14}Fe_{60}Co_{16}B_6Nb_{0.1}(AlSiCuGaGd)_{0.3}$ before and after heat treatment are presented in figures 3 and 4.

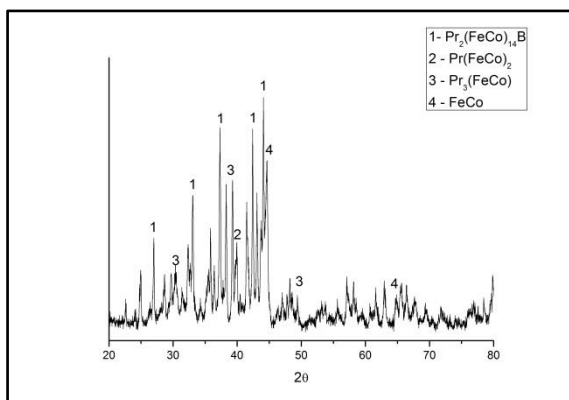


FIGURE 3: XRD pattern of the alloy $Pr_{14}Fe_{60}Co_{16}B_6Nb_{0.1}(AlSiCuGaGd)_{0.3}$ without heat treatment.

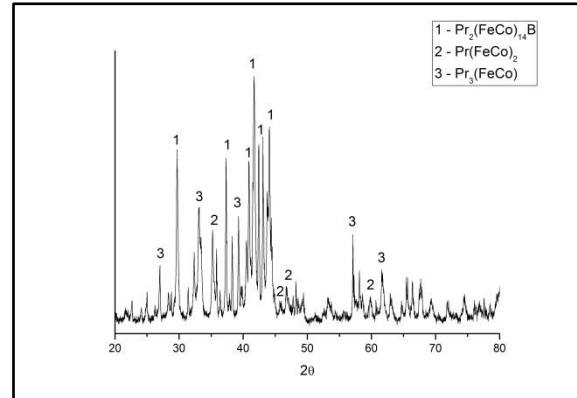


FIGURE 4: XRD pattern of the alloy $Pr_{14}Fe_{60}Co_{16}B_6Nb_{0.1}(AlSiCuGaGd)_{0.3}$ after heat treatment.

The magnets were characterized in a permeameter and the magnetic properties obtained from their demagnetization curves. Figure 5 shows the curves of the four magnets.

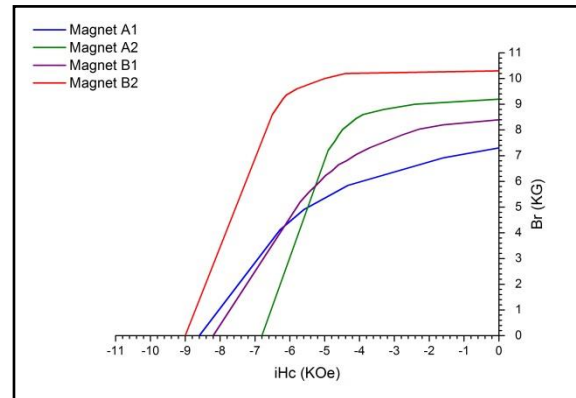


FIGURE 5: Demagnetization curves of the magnets A1, A2, B1 e B2.

The magnetic properties extracted from the demagnetization curves are shown in table 1.

TABLE 1: Magnetic properties of the magnets A1, A2, B1 and B2.

| Magnet | Br [T] | iHc [kA/m] | bHc [kA/m] | (BH) _{max} [kJ/m ³] | FQ [ratio] |
|--------|--------|------------|------------|--|------------|
| A1 | 0,73 | 684,37 | 477,46 | 86,4 | 0,40 |
| A2 | 0,92 | 541,13 | 437,68 | 147,84 | 0,60 |
| B1 | 0,84 | 652,54 | 477,46 | 102,4 | 0,41 |
| B2 | 1,03 | 716,2 | 700,28 | 204 | 0,70 |

The table results show that the magnets made with 67 wt% of the heat treated alloy (A2 and B2) had better remanence values (Br), square factor (SF), besides a maximum energy product ((BH)_{max}) approximately 50% higher compared to the magnets produced from the

mixture where the alloy was not heat treated (A1 and B2).

The magnet produced from the mixture containing the heat treated alloy and higher amount of alloying elements (B2), showed the best results in all magnetic properties. Studies indicate that certain amounts of Co and/or Ga addition increase the intrinsic coercivity (iH_c), but decrease remanence (Br), square factor (SF) and maximum energy product ($(BH)_{max}$) [9]. Other studies show that elements such as Al, Cu and Si directly influence these properties according to the contents added and combinations used [10].

4. Conclusions

From the results it is concluded that:

Heat treatment, at 1343K for 20 hours, was effective, since it eliminated the phase rich in iron ($FeCo$), as the micrographs and XRD patterns confirm.

Better magnetic properties were obtained for the magnets prepared with the mixtures where the alloys were heat treated. This indicates that the phase rich in iron is detrimental to the magnetic properties.

The magnet produced with the heat treated alloy $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}(AlSiCuGaGd)_{0.5}$, showed the best remanence ($Br = 1,03$ T), the best intrinsic coercivity ($iH_c = 716,2$ kA.m⁻³), the best maximum energy product ($(BH)_{max} = 204$ kJ.m⁻³), plus the best square factor ($SF = 0.70$).

The magnet produced with the higher content of alloying elements showed better magnetic properties compared to the magnet produced with the lower content. This indicates that the alloying elements have a direct influence in the magnetic properties [9,10].

5. Acknowledgements

The authors acknowledge IPEN for the infrastructure, CNPq for the scholarship granted, and Dr. Ricardo M. L. Neto for providing the planetary mill for sample preparation – process nº 2001/03961-4 and process nº 2015/26723-4, São Paulo Research Foundation (FAPESP).

6. References

- [1] GUTFLEISCH, O *et al.* Adv.Mater. v.23, p.821-842, 2011.
- [2] KNOBEL, M. Revista Ciência Hoje, v.36, p.18-26, 2005.
- [3] TROUT, S.R. In XVII RARE EARTH PERMANENT MAGNET WORKSHOP, p. 1-5, 2002.
- [4] WESCHENFELDER, F. *et al.* Tecnol. Metal. Mater. Miner., v. 9, p. 309-315, 2012.
- [5] POUDYAL, N.; LIU, J. P. Journal of Physics D: Applied Physics. V. 46, p. 23, 2013.
- [6] TAKIISHI, H. Estudo da Microestrutura e Propriedades de Ligas Magnéticas e Ímãs Permanentes de Terras Raras-Metais De Transição-Boro Processados Com Hidrogênio, Tese (Doutorado em Tecnologia Nuclear), Programa de Pós-Graduação em Tecnologia Nuclear, Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, São Paulo, 2001.
- [7] HARRIS, I.R.; NOBLE, C.; BAYLE, T. J. Less-Common Metal, v. 131, p. L1-L4, 1985.
- [8] TAKIISHI, H.; LIMA, L.F.C.P., FARIA, R.N. Powder Technology, v.127, p.223-225, 2002.
- [9] FARIA, R.N.; TAKIISHI, H.; LIMA, L.F.C.P.; COSTA, I. Journal of Magnetism and Materials, v.237, p.261-266, 2001.
- [10] OLIVEIRA, M.C.L.; TAKIISHI, H.; COSTA, I.; FARIA, R.N. Mater. Sci. Forum, v.170, p.530-531, 2006.