

Study of oxidation on Pr-Fe-Co-B nanopowders produced by HDDR and mechanical milling

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ABSTRACT

The aim work is focused on investigations of the oxidation products of HDDR powders followed by mechanical milling. Different compositions based on Pr-Fe-Co-B alloy following specific oxidation conditions by 200°C for 96h were analyzed. The influences of Co additions on oxidation process on Pr-Fe-B-Co powders were verified from the particles morphology, alterations on magnetic properties of the powders resulted on the oxidation process) and its stability on air (weight gain). The magnetic properties were measured using a vibrating sample magnetometer (VSM), the phases were identified by X ray diffraction (XRD) and the morphology of the particles (of the powders) was(were) obtained using a field emission gun – scanning electron microscope (SEM-FEG).

INTRODUCTION

A study about the effect of cobalt content of Pr-Fe-Co-B-Nb alloys in HDDR magnets was realized previously. Pr₁₄Fe_{75.9}Co₄B₆Nb_{0.1} HDDR powders exhibited good remanence, energy product and squareness factor (Br =840 mT, BH_{max} = 121 kJ/m³ and SF = 0.50) [1].

The degradation of Nd-Fe-B magnets has been studied due to the interest in its poor oxidation resistance [2]. At high temperatures and/ or long-term thermal aging tests, results in the formation of a layer of oxides on the surface of the magnets. It occurs due the decomposition of the Nd₂Fe₁₄B phase with the formation of Fe₃O₄ and α-Fe₂O₃ [2 – 4].

In order to improve the Rare earth – Iron – Boron (RE-Fe-B) thermal stability, the effect of additions of some elements as Co, Dy, Zr, V, Al and Cu were studied [5 – 6]. Alloys containing Cu addition seem to be very susceptible to oxidation and, a small amount of oxygen does not affect the magnetic properties [6].

Results of kinetic oxidation on Nd-Fe-B type permanent magnets (whose compositions have Al and Nb as additives) presented reduction on the degradation of the Nd₂Fe₁₄B phase due to diffusion impediment of oxygen in magnet [4].

The present work is focused on effect of Co addition on the oxidation behavior of Pr-Fe-B- Co nanopowders.

EXPERIMENTAL PROCEDURE

Pr₁₄Fe₈₀B₆ alloy in the as-cast state was submitted a hydrogenation, disproportionation, desorption and recombination (HDDR) process. Details about the preparation of the HDDR powders were described in previous papers [7 – 8]. Alfa-iron, cobalt and iron-boron in powder form were added to the powders resulting of HDDR process according the intended stoichiometric composition.

Different compositions based on Pr-Fe-B-Co-Nb alloys studied in this paper are summarized in Table 1.

Table 1 – Compositions of the prepared samples studied in this work.

COMPOSITION	SAMPLE - before oxidation process	SAMPLE - after oxidation process
$\text{Pr}_8\text{Fe}_{81.94}\text{Co}_4\text{B}_6\text{Nb}_{0.06}$	Co_4	Co_4 (96h – 200°C)
$\text{Pr}_8\text{Fe}_{77.94}\text{Co}_8\text{B}_6\text{Nb}_{0.06}$	Co_8	Co_8 (96h – 200°C)
$\text{Pr}_8\text{Fe}_{75.94}\text{Co}_{10}\text{B}_6\text{Nb}_{0.06}$	Co_{10}	Co_{10} (96h – 200°C)
$\text{Pr}_8\text{Fe}_{69.94}\text{Co}_{16}\text{B}_6\text{Nb}_{0.06}$	Co_{16}	Co_{16} (96h – 200°C)

The mixed powders were inserted in a stainless steel grinding bowl with cyclohexane and oleic acid and them were mechanically milled (FRITSCH – Pulverisette 7) by 5 hours at 900 rpm.

To investigate the oxidation of the material an amount of each powder composition was oxidized on specific conditions (200°C for 96 hours on air).

The magnetic properties of the powders were measured in vibrating sample magnetometer (VSM), x-ray patterns of oxidized and non-oxidized powders were collected in a RIGAKU diffractometer. The microstructures of the samples were carried out using a field emission gun – scanning electron microscope (SEM-FEG).

RESULTS

The percentage weight gains of the powders oxidized at 200°C during 96 hours were showed in Table 2. Increasing the cobalt addition on Pr-Fe-B-Nb alloys decreases the oxidation of the samples. The rate of weight gains of Co_4 was 6.31% while Co_{16} powder was 2.05%. Additions of cobalt improved the resistance/ stability of processed powders to oxidizing atmosphere.

Table 2 – Weight gain in percentage of the oxidized powders.

SAMPLE	WEIGHT GAIN (%)
Co_4 (96h – 200°C)	6.31
Co_8 (96h – 200°C)	3.32
Co_{10} (96h – 200°C)	2.97
Co_{16} (96h – 200°C)	2.05

As expected oxidation of the HDDR powders milled mechanically suffers reduction on their magnetic properties. Table 3 presents decrease on magnetic properties between the samples oxidized and non-oxidized (iH_c - intrinsic coercivity, M_r – remanent magnetization and, M_s – saturation magnetization).

Table 3 – Magnetic properties of Pr-Fe-Co-B nanopowders before and after oxidation test (96h at 200°C).

SAMPLE	iH_c (Oe)	M_r (emu/g)	M_s (emu/g)
Co_4	166.00	17.47	126.38
Co_4 (96h – 200°C)	59.00	9.16	113.14
Co_8	100.00	11.65	123.97
Co_8 (96h – 200°C)	87.00	8.15	115.80
Co_{10}	151.00	17.34	118.14
Co_{10} (96h – 200°C)	66.00	6.97	105.34
Co_{16}	136.00	13.41	90.16
Co_{16} (96h – 200°C)	20.00	8.03	85.48

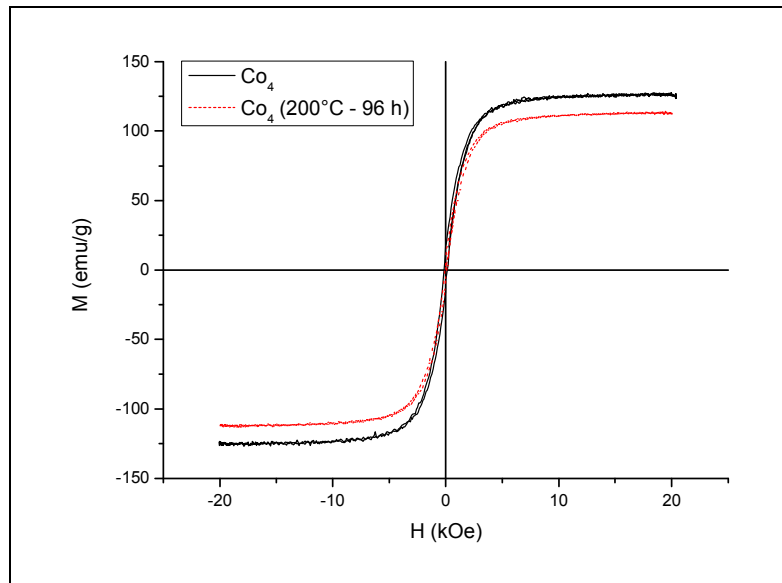
According to the Table 3 (and Figure 1) can be noticed that all magnetic properties decreases after oxidation. It happens because the matrix phase, $\text{Pr}_2(\text{FeCo})_{14}\text{B}$, existing in Pr-Fe-B-Co-Nb powders decreases harshly with the presence of oxidizing atmosphere promoting the formation of several types of iron and praseodymium oxides undesirable.

Comparative hysteresis loops obtained by vibrating sample magnetometer are shown in Figure 1(a – b). In Figure 1a the hysteresis loops compares the magnetic properties of Co_4 (4% at. Co) samples before and after the oxidation while the Figure 1b is corresponding to Co_{16} (16% at. Co). For both graphics the dashed lines are corresponding to samples oxidized while the solid lines are corresponding to non-oxidized samples.

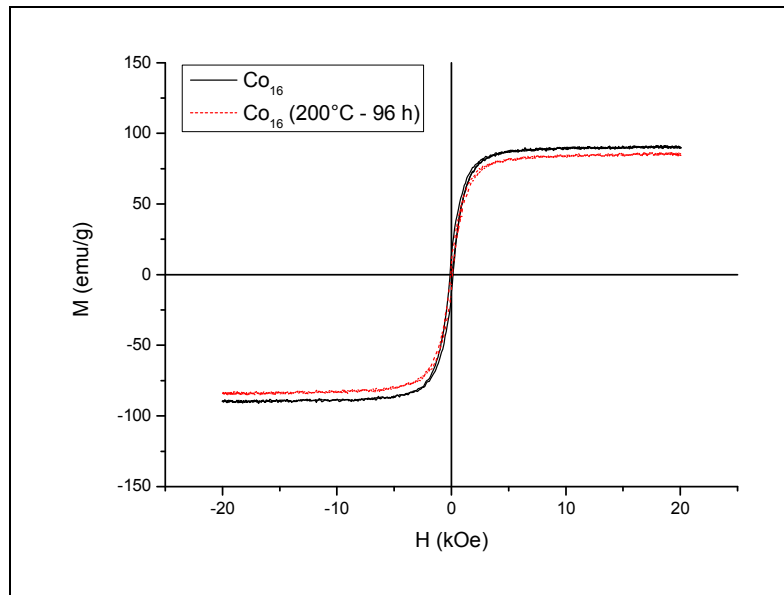
A previous study suggested that Co addition on Pr-Fe-B magnets cause changes in the microstructures. Alloys with 4% to 10% Co at. additions presented two phases: $\text{Pr}_2(\text{FeCo})_{14}\text{B}$ and $\text{Pr}_3(\text{FeCo})$, which is Pr rich. Increasing cobalt content in the compositions (12% to 16% Co at.) occurs the formation of an intergranular phase, $\text{Pr}(\text{FeCo})_2$, known as laves phase [9].

Increasing the proportion of the laves phase and consequent reduction of the matrix and Pr-rich phases in the microstructure presents the decrease in the formation oxides. Is well known that the oxidation of RE-Fe-B powders exhibit two stages: a quick oxidation of RE rich phase followed by the oxidation of $\text{RE}_2\text{Fe}_{14}\text{B}$ grains [10]. Then it can be considered that there is a decrease in phases that are oxidized initially occur a decrease in mass gain of samples exposed to 200°C for 96 hours.

The XRD patterns of oxidized powders of the compositions studied are shown in Figure 2. All peaks in these patterns are reasonably broad, indicating poor crystallization of the phases. The pattern of Co_4 (96h – 200°C) presents peaks of $\alpha\text{-Fe}$ and $\alpha\text{-Fe}_2\text{O}_3$. The absence of peaks of $\text{Pr}_2\text{Fe}_{14}\text{B}$ in Co_4 (96h – 200°C) patterns indicates the complete oxidation of this hard magnetic phase.



1(a)



1(b)

Figure 1 - Comparative hysteresis loops of (a) 4% at. Co addition and, (b) 16% at. Co addition. The solid lines represent the samples of nanomagnetic powders without oxidation and the dash lines the samples oxidized.

The pattern of Co_8 (96h – 200°C) present a decrease of peaks intensity but are still found α -Fe and α - Fe_2O_3 phases.

Adding cobalt in the alloy in 10% at. the XRD pattern (named Co_{10} (96h – 200°C)) presented only two distinct phases: α -Fe and $\text{Pr}_2\text{Fe}_{14}\text{B}$.

The pattern of Co_{16} (96h – 200°C) sample showed peaks with low intensity and very broad. Could be identified the peaks of α -Fe and $\text{Pr}_2\text{Fe}_{14}\text{B}$.

It was verified that with an increase of Co addition in the samples occurred a decrease in the oxides formation and the appearance of $\text{Pr}_2\text{Fe}_{14}\text{B}$ phase.

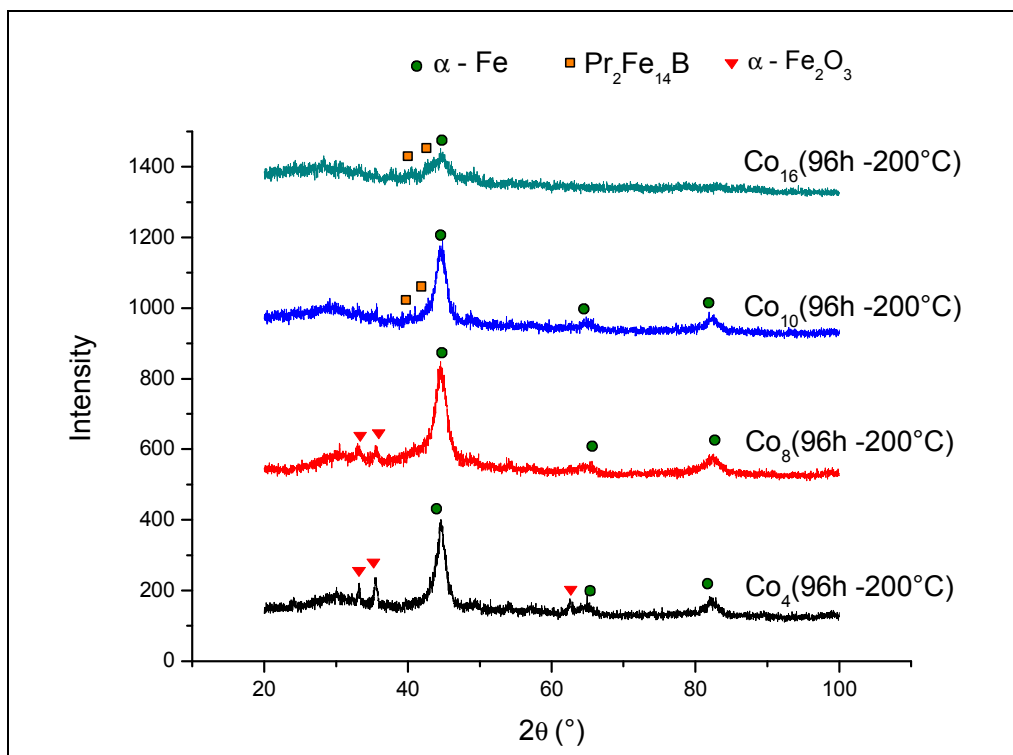


Figure 2 – XRD patterns of the oxidized nanomagnetic powders.

SUMMARY

Increasing the cobalt addition on Pr-Fe-B-Nb alloys decreases the oxidation of the samples. Composition with 4% at. cobalt presented 6.31% of weight gain and the composition with 16% at. cobalt presented 2.05% of weight gain. All samples had a decrease in their magnetic properties after oxidation on air during 96 h at 200°C. XRD patterns have been shown that the magnetic phase Pr₂Fe₁₄B was detected in samples with 10 and 16% at cobalt additions.

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