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Observation of hydrogen induced intermediate borides in PrFeB based alloys by Mössbauer effect spectroscopy

F.D. Saccone[a,]*, C.E. Rodríguez Torres[a], F.H. Sánchez[a], O. Gutfleisch[b]

[a] *Dept. de fisica Facultad de ciencias exactas, Instituto de Física de La Plata, Univ. nacional de la Plata, CC 67, 1900 La Plata, Argentina*
[b] *IFW Dresden, P.O. Box 270016, 01171 Dresden, Germany*

Abstract

In the present work, a quantitative analysis of the phase compositions by Mössbauer effect spectroscopy of solid and conventional hydrogen disproportionated $Pr_{13.7}Fe_{80.3}B_{6.0}$ and $Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_{6.0}$ alloys was carried out. Significant amounts of intermediate borides t-Fe_3B and $Pr(Fe,Co)_{12}B_6$ were detected after solid hydrogen disproportionation treatment in $Pr_{13.7}Fe_{80.3}B_{6.0}$ and $Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_{6.0}$ alloys, respectively. After conventional hydrogenation–disproportionation–desorption–recombination treatment these phases were not detected and in no case residual $Pr_2Fe_{14}B$-phase was found. It was observed that the amount of intermediate borides after disproportionation can be correlated with the degree of texture after recombination at various temperatures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PrFeB hard magnets; HDDR process; Magnetic anisotropy

PrFeB-based systems have proved to be very suitable for texturing via conventional hydrogenation–disproportionation–desorption–recombination (HDDR) processing [1]. Various models for elucidating the mechanism of the inducement of texture have been proposed [2]. The presence of intermediate boride phases such as t-Fe_3B and/or the additions of elements such as Co, Ga, Zr, etc., have been reported as being relevant for magnetic anisotropy preservation of recombined NdFeB-phases [3,4]. Only recently, interest has arisen in PrFeB-type alloys and it has been reported that these HDDR processed alloys could exhibit a high degree of anisotropy [5,6].

In the present work, in order to deepen the understanding of texture inducement in $Pr_2Fe_{14}B$-type alloys, a quantitative analysis of the phase compositions of solid hydrogen disproportionated $Pr_{13.7}Fe_{80.3}B_{6.0}$ (Alloy A) and $Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_{6.0}$ (Alloy B) samples was undertaken. Furthermore, a correlation of the boride contents with the demagnetization behavior of the recombined cold compacted magnets for different solid HDDR processing temperatures [7] was attempted.

These samples were disproportionated by heating them in vacuum to temperatures of 800°C and 875°C at which a hydrogen pressure of 0.8 bar was applied for 30 or 15 min. For recombination the hydrogen pressure was lowered after hydrogenation and the powder was held for 30 min at 0.1 bar, followed by a final desorption stage of 5 min under

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*Corresponding author. Fax: +54-221-425-2006.
E-mail address: saccone@fisica.unlp.edu.ar (F.D. Saccone).

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continuous pumping. For comparison, conventional disproportionation has been carried out under 0.8 bar hydrogen pressure at 800°C for 30 min.

Powders were quenched from the disproportionated state and the quantification of the present phases was made by ^{57}Fe Mössbauer effect (ME) spectroscopy. Details of the experimental setup are given elsewhere [8].

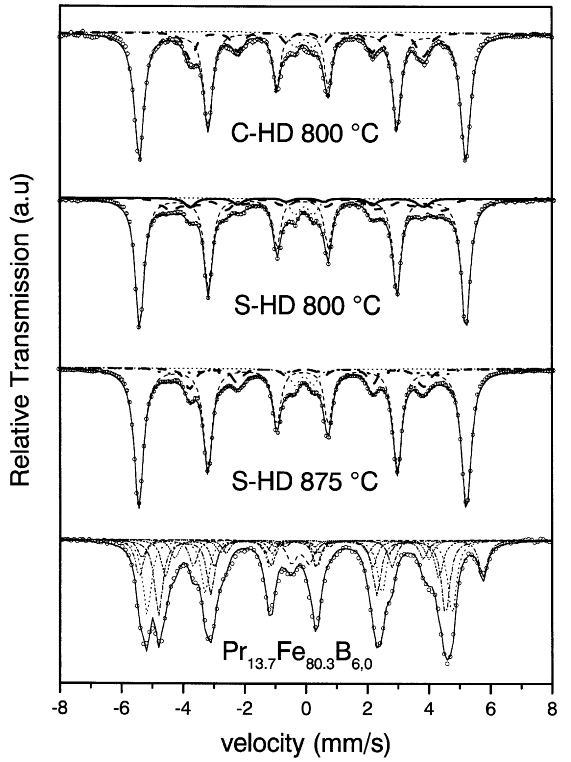

Fig. 1. ME spectra of ingot and HD alloy A ($Pr_{13.7}Fe_{80.3}B_{6.0}$), disproportionated by 30 min.

Magnetic properties of the recombined samples were studied by vibrating sample magnetometry (VSM) with a maximum field of 8 T at room temperature. Prior to the VSM measurements the powders were aligned in a magnetic field of 2 T during cold compaction.

Fig. 1 shows the ME spectra of the A ingot alloy and the samples S-HD 800°C, S-HD 875°C and C-HD 800°C, 30 min. The spectrum of the starting alloy was fitted with the superposition of six magnetic sextets whose relative intensities were constrained to be equal to the relative abundance of the crystallographic non-equivalent iron sites of the ϕ-$Pr_2Fe_{14}B$ structure and with a central paramagnetic doublet consistent with the presence of about 5% of Fe in the η-$PrFe_4B_4$-phase ($\delta = 0.049$ mm/s, $\Delta = 0.59$ mm/s). The corresponding spectra of the disproportionated samples were fitted with the superposition of η-phase, t-Fe_3B, Fe_2B and α-Fe spectra. No residual ϕ-phase was detected after disproportionation in any case. The relative weight percentage calculated assuming equal recoil free fractions for all structural sites based on the known samples stoichiometry, are shown in Table 1. The S-HD 800°C sample has 6.2 wt% of metastable t-Fe_3B which is less than the amount of Fe_2B, this relation reverts for the 875°C treatment. This relative proportion was confirmed by Rietveld analysis of the XRD pattern (see Ref. [5]) but the obtained XRD fractions are smaller than the ME ones. In general, XRD and ME agree

Table 1
Calculated wt% from Mössbauer measurements in C-HD and S-HD alloy A ($Pr_{13.7}Fe_{80.3}B_{6.0}$) and alloy B ($Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_{6.0}$)

Alloy A	α-Fe	t-Fe_3B	Fe_2B	$PrFe_4B_4$	PrH_{2+x}
S-HD 875°C, 15 min	53.1±0.5	12.4±0.3	5±0.1	6.6±0.1	22.9±0.5
S-HD 875°C, 30 min	52.6±0.5	13.5±0.3	4.6±0.1	6.3±0.1	23.0±0.5
S-HD 800°C, 30 min	55.6±0.6	6.2±0.2	9.3±0.2	5.7±0.1	23.2±0.5
C-HD 800°C, 30 min	56.2±0.6	—	14.7±0.3	6.0±0.1	23.1±0.5

Alloy B	α-(Fe, Co)	$Pr(Fe, Co)_{12}B_6$	$(Fe, Co)_2B$	PrH_{2+x}
S-HD 875°C, 30 min	55.6±0.6	14.5±0.3	3.8±0.1	25.9±0.5
S-HD 800°C, 30 min	57.3±0.6	6.1±0.1	7.8±0.2	28.9±0.6
C-HD 800°C, 30 min	60.5±0.6	1.3±0.1	13.2±0.3	24.9±0.5

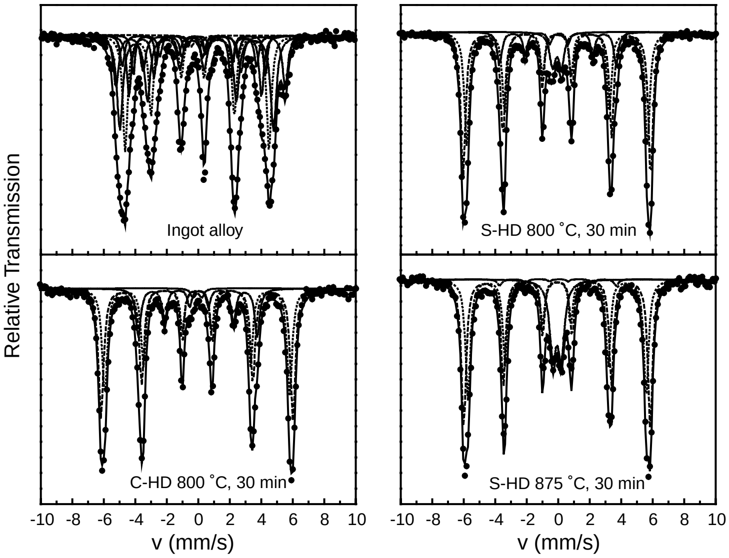

Fig. 2. ME spectra of ingot and HD alloy B ($Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_{6.0}$), disproportionated by 30 min.

in the identification of the present phases, but the quantification of t-Fe_3B, Fe_2B, $PrFe_4B_4$ are smaller when determined by XRD probably due to very small size of the boride grains. The relative fractions of the present phases after the S-HD 875° 15 min treatment are almost the same as the 30 min one.

The Fe_3B content in the PrFeB-alloy after disproportionation are of the order of those observed in NdFeB-alloys [9]. In C-HD 800°C the only detected boride was Fe_2B.

In the case of the B alloy (see Fig. 2) the S-HD samples were fitted with three magnetic interactions, two of them were assigned to α-(Fe, Co) and the remaining one to $(Fe, Co)_2B$, and a paramagnetic doublet with hyperfine parameters ($\delta = 0.032$ mm/s, $\Delta = 0.56$ mm/s) very close to those of the η-phase. The relative fraction (see Table 1) of the last phase is maximum for S-HD at 875°C (14.5 wt%), smaller for S-HD at 800°C (6.1 wt%) and practically non-existent for C-HD at 800°C. XRD results did not reveal the presence of $PrFe_4B_4$, instead, an intermediate boride phase $Pr(Fe, Co)_{12}B_6$ was identified. The relative fractions determined by Rietveld analysis agree with those determined by ME for the above-mentioned paramagnetic interaction. Therefore, the doublet observed in the ME spectrum was assigned to this boride. This phase were also detected in ME spectra of C-HD samples of alloys with the same composition treated at 860 and 920°C [10].

Fig. 3 shows easy and hard axis demagnetization curves for the two alloys after solid-HDDR processing. It can be seen that, in both type of alloys, the induced texture is more pronounced in the sample S-HDDR at 875°C, less in the 800°C sample. Under the specific processing conditions used here, the conventionally processed material is isotropic. This could be related to the relative amount of intermediate boride phases obtained after disproportionation. It appears that: the higher the amount of Fe_3B or $Pr(Fe, Co)_{12}B_6$ in the disproportionated state, the higher the degree of texture observed in the final state.

The correlation between the resulting coercivities and remanences with the amount of intermediate boride is not straightforward. While the amount of $Pr(Fe, Co)_{12}B_6$ coincides with an increment of both coercivity and remanence of B alloy, a higher remanence was found after the 875°C treatment (higher t-Fe_3B content) for A but now coinciding with a decrease of coercivity. It seems that t-Fe_3B had a beneficial effect on

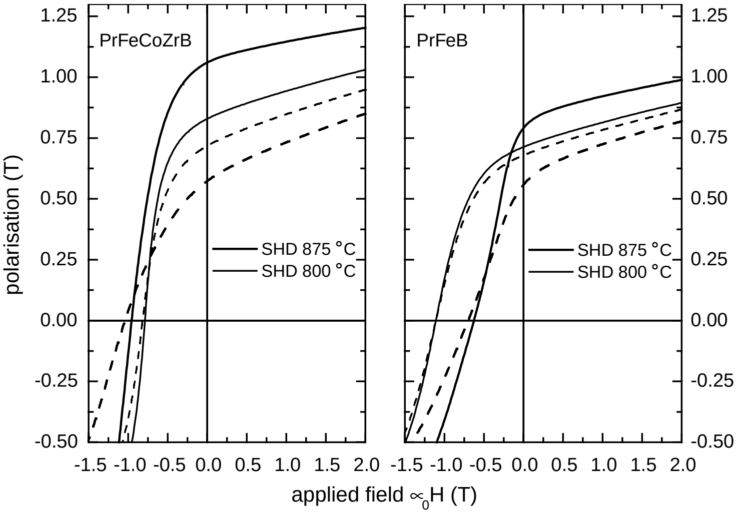

Fig. 3. Comparison of easy-axis and hard-axis demagnetization curves for magnets made from S-HDDR treated $Pr_{13.7}Fe_{80.3}B_{6.0}$ (alloy A) and $Pr_{13.7}Fe_{63.5}Co_{16.7}Zr_{0.1}B_{6.0}$ (alloy B) powders. Dashed lines correspond to hard-axis demagnetization curves.

the texture inducement with the drawback of difficulties in controlling grain growth at higher processing temperatures (875°C) in the ternary system [7].

In summary, *t*-Fe_3B was detected, after solid hydrogen disproportionation treatment, only in A; while $Pr(Fe, Co)_{12}B_6$ was observed in B alloy. $Pr(Fe, Co)_{12}B_6$ percentages as measured by XRD and ME agree within the experimental error, but those of *t*-Fe_3B, Fe_2B, $PrFe_4B_4$ are higher when determined by ME. Most probably this difference is due to a very small size of the boride grains. In any case, neither after solid nor after conventional disproportionation residual $Pr_2Fe_{14}B$-phase was observed in either alloy. It was also found that the amount of intermediate borides after the disproportionation could be correlated with the degree of texture in the recombined material.

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