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The effect of cobalt content on the microstructure of Pr–Fe–Co–B–Nb alloys and magnetic properties of HDDR magnets

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Abstract

This paper reports the results of investigations carried out to determine the microstructure and magnetic properties of some cast and homogenized praseodymium-based alloys and magnets represented by the formula $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$. Permanent magnets were prepared from cast and annealed alloys using the hydrogenation, disproportionation, desorption and recombination process. The effect of cobalt content on the magnetic properties of these magnets was investigated. Cobalt has a significant effect on the magnetic behaviour of these alloys. Microstructural examinations revealed that the grain size of the matrix phase increased with increasing cobalt content in the Pr-based alloys and niobium had a grain-refining role.

Keywords: Pr-based alloys; magnetic materials; hydrides; magnetic properties

1. Introduction

Permanent magnet powders prepared by the hydrogenation, disproportionation, desorption and recombination (HDDR) process are high coercivity materials and these can be obtained by exposing Nd-based alloys to hydrogen at elevated temperatures (examples in Refs. [1–4]). Cobalt free Pr-based powders have been produced via the HDDR process, but with inferior magnetic properties, compared to Nd-based materials [5]. PrFeCoBGaZr-type HDDR powders with good remanence have also been reported [6]. The intrinsic coercivity in these materials is still quite poor. Recently, it was shown that powders based on the composition $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6M_{0.1}$ (M = Zr or Nb), with good remanence ($B_r \sim 1000\,\text{mT}$) and reasonable coercivity (${}_iH_c \sim 790\,\text{k A m}^{-1}$) can be produced by the HDDR process ($pH_2 = 0.1\,\text{MPa}$) [7–10]. This paper reports the results of further work carried out on $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type alloys (where $x = 0$, 4, 8, 10, 12, 16). This investigation was undertaken to optimise the cobalt content with respect to the magnetic properties of the HDDR magnets. The microstructures of the magnetic alloys were observed with a scanning electron microscope (SEM) and the phase compositions were determined with the aid of an energy

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Table 1
Composition of the as-cast alloys

Nominal composition (at%)	Specified and analysed composition (wt%)					
	Pr	Fe	Co	B	Nb	Al
$Pr_{14}Fe_{80}B_6$	30.32	68.68	—	1.00	—	—
	30.30	68.62	—	0.99	—	0.09
$Pr_{14}Fe_{79.9}B_6Nb_{0.1}$	30.31	68.55	—	1.00	0.14	—
	30.11	68.68	—	0.97	0.14	0.10
$Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$	30.25	65.00	3.61	1.00	0.14	—
	30.05	65.16	3.58	0.97	0.15	0.09
$Pr_{14}Fe_{71.9}Co_8B_6Nb_{0.1}$	30.19	61.46	7.22	0.99	0.14	—
	30.29	61.36	7.15	0.96	0.15	0.09
$Pr_{14}Fe_{69.9}Co_{10}B_6Nb_{0.1}$	30.47	59.39	9.01	0.99	0.14	—
	30.16	59.51	9.03	1.02	0.16	0.12
$Pr_{14}Fe_{67.9}Co_{12}B_6Nb_{0.1}$	30.14	57.93	10.80	0.99	0.14	—
	30.14	57.80	10.83	0.98	0.15	0.10
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	30.08	54.41	14.38	0.99	0.14	—
	30.35	54.11	14.34	0.96	0.14	0.10

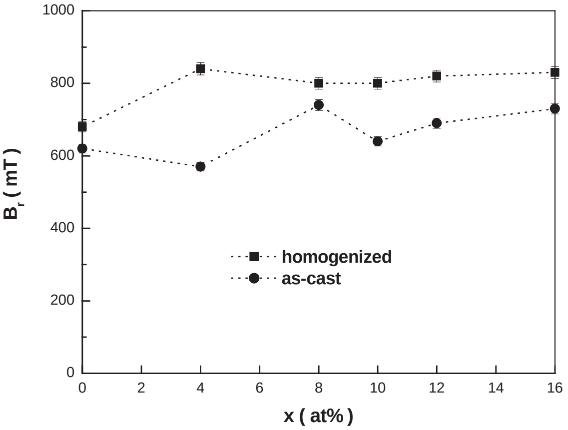

Fig. 1. Remanence versus cobalt content for $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type HDDR magnets.

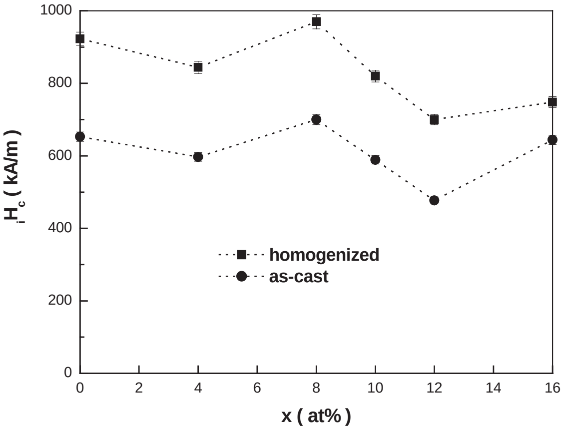

Fig. 2. Coercivity versus cobalt content for $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type HDDR magnets.

dispersive X-ray (EDX) spectrometer system coupled to the SEM.

2. Experimental procedure

Various commercial alloys in the as-cast state and after annealing in vacuum at 1100°C for 20 h were studied. The chemical analyses of the as-cast alloys are given in Table 1. All the alloys contain about 0.1 wt% aluminium as an impurity (as per the supplier's specification). The niobium-free alloy was included in this study for comparison. The following procedure was adopted to produce the Pr-based magnets via the HDDR process [7–10]. The as-cast and annealed alloys were crushed into coarse lumps and 9 g batches were placed in the HDDR reactor. This reactor was then evacuated to the backing-pump pressure ($\sim 10^{-1}$ mbar) and hydrogen introduced until the pressure varied between 0.08 and 0.25 MPa (0.8–2.5 bar). The temperature of the reactor was held at 100°C for 30 min to provide sufficient time for the hydrogen decrepitation (HD) reaction to go to completion. The reactor was then heated to 770°C at 15°C/ min and further up to the desorption temperature (860°C) at 5°C/ min, with a dwell time of 15 min prior to desorption [8]. Subsequent desorption and recombination was carried out under vacuum at the same temperature until a pressure of 10^{-1} mbar was achieved (~ 10 min). Subsequent rapid cooling of the material was carried out by removing the furnace from the HDDR reactor and by coupling a water-cooled copper coil to the reactor tube.

The resultant powder was crushed in air until all the material passed through $a < 106\,\mu\text{m}$ sieve. The fine powder was subsequently encapsulated in a small cylindrical rubber bag, pulsed in a magnetic field of 6.0 T and pressed isostatically at 200 MPa. The resultant green compacts were consolidated by placing wax in the bag and heating to 100°C, to enable the molten wax to penetrate the HDDR powder compact. The mixture was then allowed to cool to room temperature and the excess wax removed to yield a cylindrical magnet.

Magnetic characterisation of the HDDR magnets was carried out using a permeameter. Measurements were performed after saturation in a pulsed field of 6.0 T. Remanence values have been normalized assuming 100% density for the HDDR sample, and by also considering a linear relationship between density and remanence. Microstructural characterization of the alloys was carried out with the aid of a SEM.

3. Results and discussion

Variation in remanence of HDDR magnets, produced from as-cast and annealed Pr-based alloys, as a function of cobalt content is shown in Fig. 1. Good remanence values were achieved in samples prepared from annealed Co-containing alloys. In the presence of 4.0 at% Co, the remanence increased from 790 to 840 mT. Higher Co contents produced a slight decrease in remanence. Overall, and as expected, the remanence of

Table 2
Magnetic properties of Pr-type HDDR magnets (error: ±2%)

Composition	Alloy condition	Br (mT)	${}_iH_c$ (kA/m)	${}_bH_c$ (kA/m)	$(BH)_{max}$ (kJ/m^3)	SF (ratio)
$Pr_{14}Fe_{80}B_6$	As-cast	620	748	366	59	0.28
	Homogenised	680	923	462	81	0.29
$Pr_{14}Fe_{79.9}B_6Nb_{0.1}$	As-cast	620	653	382	60	0.32
	Homogenised	790	923	477	114	0.39
$Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$	As-cast	570	597	334	49	0.24
	Homogenised	840	844	501	121	0.50
$Pr_{14}Fe_{71.9}Co_8B_6Nb_{0.1}$	As-cast	740	700	382	76	0.24
	Homogenised	800	970	493	111	0.34
$Pr_{14}Fe_{69.9}Co_{10}B_6Nb_{0.1}$	As-cast	640	589	311	52	0.19
	Homogenised	800	820	477	107	0.46
$Pr_{14}Fe_{67.9}Co_{12}B_6Nb_{0.1}$	As-cast	690	477	279	54	0.17
	Homogenised	820	700	541	113	0.43
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	As-cast	730	644	382	70	0.20
	Homogenised	830	748	477	101	0.34

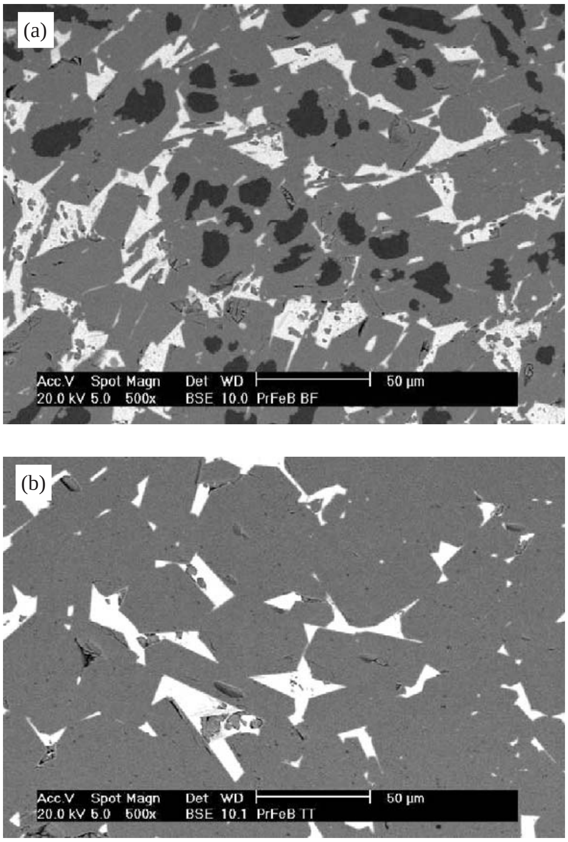

Fig. 3. Back-scattered electron image of the $Pr_{14}Fe_{80}B_6$ alloy in the (a) as-cast and (b) annealed condition.

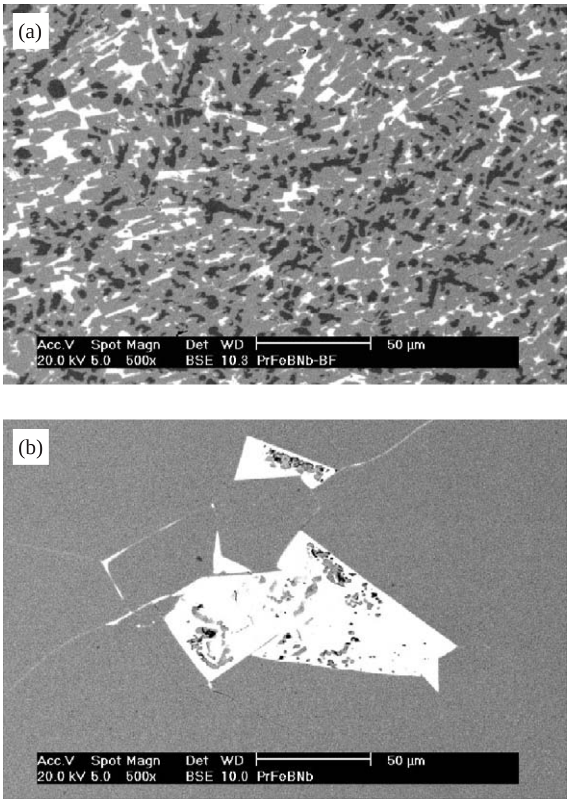

Fig. 4. Back-scattered electron image of the $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ alloy in the (a) as-cast and (b) annealed condition.

the HDDR magnets produced from the alloy in the annealed condition was higher than that of magnets produced from the as-cast alloy. The large variations in remanence values of HDDR magnets produced from the as-cast alloys can be attributed to the heterogeneous condition of the alloys.

Fig. 2 shows the variation in intrinsic coercivity of HDDR magnets produced from as-cast and annealed Pr-based alloys as a function of cobalt content. Good intrinsic coercivity values were achieved in samples prepared using the annealed alloys. In the presence of 8.0 at% cobalt, a magnet with the best intrinsic coercivity (970 kA/m) was obtained. At higher Co contents this magnetic property decreased. Again, as expected, the coercivity of HDDR magnets produced from annealed alloys was higher than in magnets produced from as-cast alloys. It was also noted that the HDDR magnet produced using the Co-free alloy in the annealed condition presented good intrinsic coercivity (923 kA/m).

The magnetic properties of all the magnets produced with alloys in the as-cast and annealed conditions are shown in Table 2. The best energy product (121 kJ/m^3) was observed in the magnet containing 8 at% cobalt, which was prepared from an aligned HDDR powder and an annealed precursor material. It is worth noting that the $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ magnet also showed a good energy product value (114 kJ/m^3). Niobium addition increased the remanence from 680 to 790 mT in HDDR magnets prepared from annealed Co-free alloys but had no effect on $_iH_c$ (a decrease in $_iH_c$ was observed for that in the as-cast state).

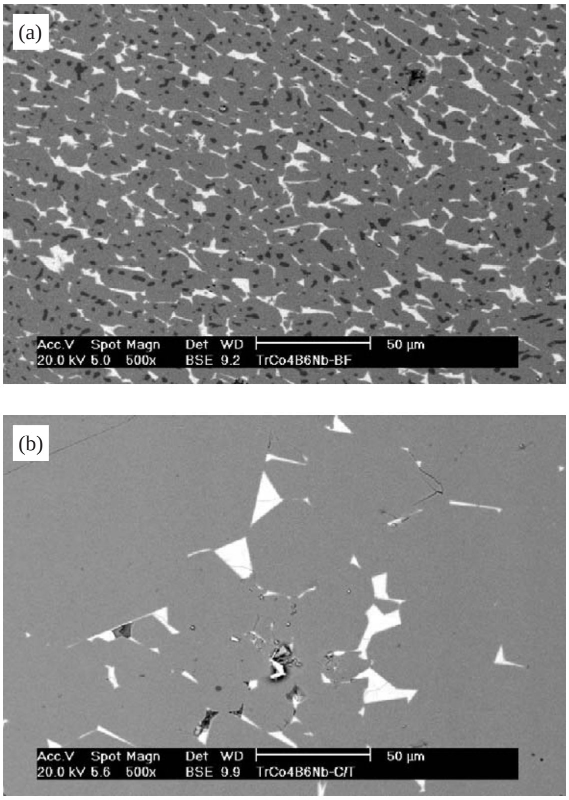

Fig. 5. Back-scattered electron image of the $Pr_{14}Fe_{75,9}$-$Co_4B_6Nb_{0,1}$ alloy in the (a) as-cast and (b) annealed condition.

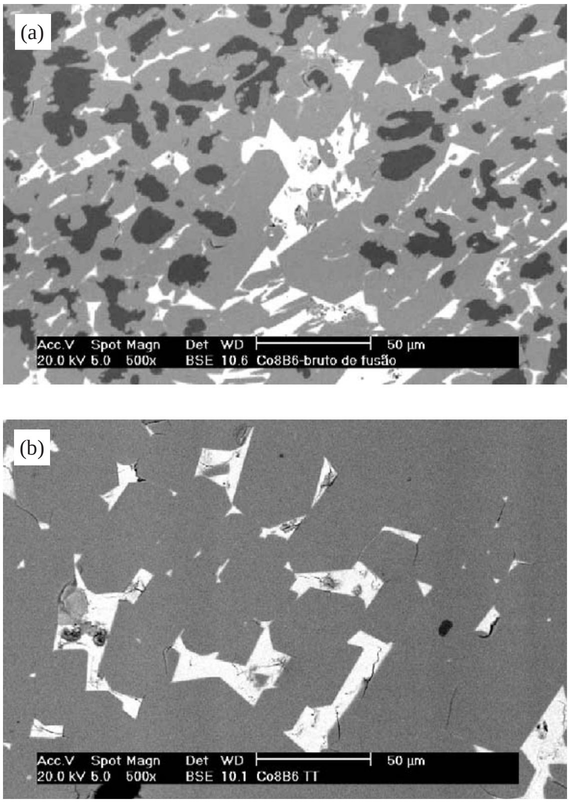

Fig. 6. Back-scattered electron image of the $Pr_{14}Fe_{71,9}$-$Co_8B_6Nb_{0,1}$ alloy in the (a) as-cast and (b) annealed condition.

The highest inductive coercivity was achieved in the $Pr_{14}Fe_{67.9}Co_{12}B_6Nb_{0.1}$ HDDR magnet (541 kA/m). The best squareness factor (SF = 0.50) was achieved in the magnet containing 8 at% cobalt, which was also prepared from an annealed alloy. The $Pr_{14}Fe_{69.9}Co_{10}B_6Nb_{0.1}$ HDDR magnet also showed a reasonable squareness factor (0.46).

Back-scattered electron images of the as-cast and annealed Pr-based alloys are shown in Figs. 3–9. It can be seen clearly that annealing at 1100°C for 20 h was quite effective in homogenizing all the alloys. Free iron (dark phase) was completely eliminated from the interior of the matrix phase grains (dark grey phase). It can also be clearly seen that niobium addition had a refining effect on the as-cast alloy. The refining effect is not evident in alloys with Co more than 4 at%. Nevertheless, cobalt addition up to 8 at% has a beneficial effect on the intrinsic coercivity. The Curie temperature of $Pr_2Fe_{14}B$ increases with the Co content, at about 11°C per at% [9] and this could be a favourable factor for additions beyond 8 at% of Co to these magnetic alloys. Increase in corrosion resistance could be another factor in favour of addition of higher amounts of Co. Further studies are being carried out to determine the effect of cobalt on the corrosion behaviour of these Pr-based alloys.

The composition of the various phases in the $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ alloy, both in the as-cast condition and annealed, are presented in terms of the ratio Pr:Fe:Co in Table 3. Cobalt was observed to substitute Fe in the matrix phase. The Pr:Fe:Co ratio is approximately 2:11:2.6 and very close to that reported in a previous study (2:10:2.3) [10] for a Zr-containing alloy ($Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$). Zirconium and niobium seem to have distinct

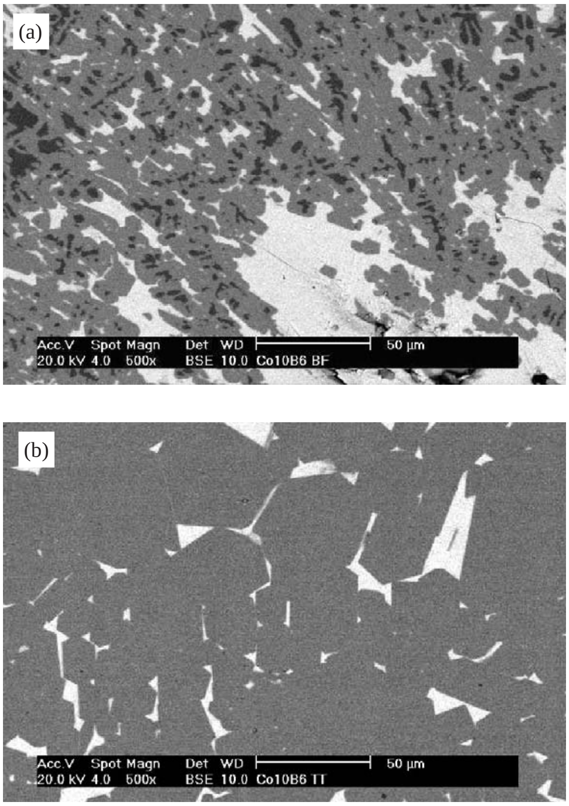

Fig. 7. Back-scattered electron image of the $Pr_{14}Fe_{69,9}$-$Co_{10}B_6Nb_{0,1}$ alloy in the (a) as-cast and (b) annealed condition.

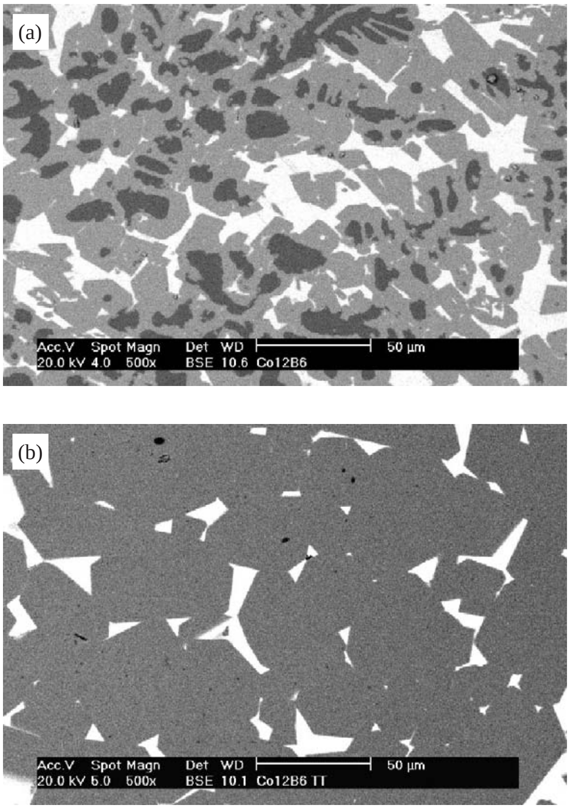

Fig. 8. Back-scattered electron image of the $Pr_{14}Fe_{67,9}$-$Co_{12}B_6Nb_{0,1}$ alloy in the (a) as-cast and (b) annealed condition.

influence in these alloys. The former appears to inhibit grain growth during heat treatment whereas the latter appears to control grain growth more effectively during the disproportionation and recombination stages of the HDDR process [11]. A small change in composition of the matrix phase was observed, as a result of the heat treatment and this was not observed in the previous investigation [10]. As shown recently [12], small differences in chemical composition can be observed with a SEM fitted with an EDX system. In all alloys, in the as-cast condition, iron and cobalt were observed in the dark dendritic phase (D), with variable Fe/Co ratio. The white (W) and grey (G) phases have been already identified [10,13] as Nd_3Co and $Nd(Fe,Co)_2$ (Laves phase), respectively. Recently, in an investigation where the effect of disproportionation of powders based on the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ alloy were studied using X-ray diffraction and Mössbauer spectroscopy, it was reported that a boride phase $Pr(Fe,Co)_{12}B_6$ is present when the alloys are disproportionated at or above 860°C [14]. Also according to this study, after recombination, this phase is still present in the early stages and it could play a role in inducing textures in the material upon further treatment. This phase disappears with increase in duration of the recombination treatment. Very recently, significant amounts of intermediate borides t-Fe_3B and $Pr(Fe,Co)_{12}B_6$ have been detected after solid hydrogen disproportionation treatment in $Pr_{13.7}Fe_{80.3}B_6$ and $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ alloys [15]. Further microstructural investigation is underway to determine the effect of cobalt on the morphology of the HDDR powder.

Table 3
Composition determined by EDX in the hard magnetic matrix phase (ϕ), the gray phase, the white phase and the dark phase on the $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ alloy, before and after annealing (error bars = ±2 standard deviation; refer to Fig. 9 to identify the phases)

Alloy condition	Phase	Identification	Pr (at%)	Fe (at%)	Co (at%)
As-cast	$Pr_2(FeCo)_{14}B$	ϕ	12.8 ± 1.1	70.8 ± 0.5	16.4 ± 1.2
	$Pr(FeCo)_2$	G	39.7 ± 0.8	19.3 ± 1.4	41.0 ± 1.0
	$Pr_3(FeCo)$	W	68.8 ± 0.7	3.4 ± 3.0	27.8 ± 1.5
	Fe Co	D	<1	87.2 ± 0.4	11.9 ± 1.3
Annealed	$Pr_2(FeCo)_{14}B$	ϕ	12.3 ± 0.6	70.1 ± 0.5	17.6 ± 0.9
	$Pr(FeCo)_2$[a]	G	34.5 ± 0.7	27.9 ± 1.1	37.6 ± 0.9
	$Pr_3(FeCo)$	W	69.5 ± 0.5	2.4 ± 1.0	28.1 ± 0.8

[a] Found only in the alloy with 16 at% Co.

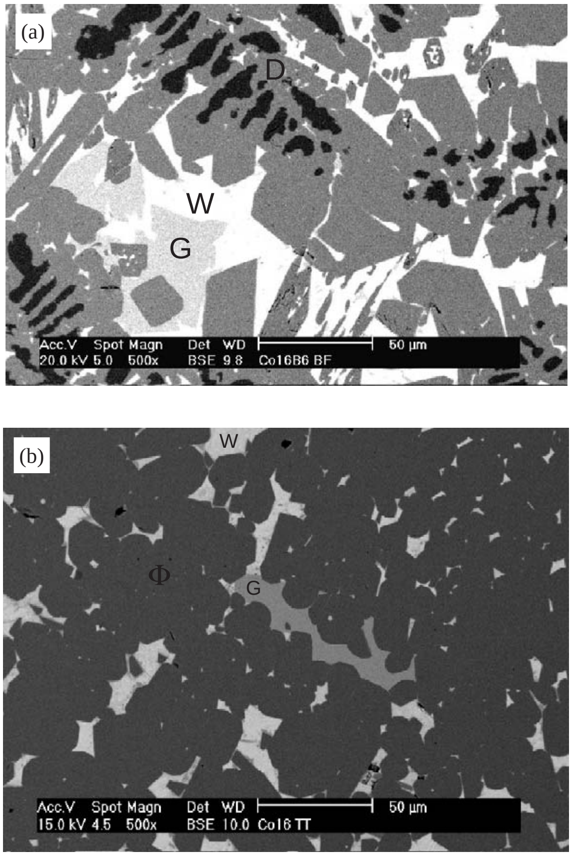

Fig. 9. Back-scattered electron image of the $Pr_{14}Fe_{63,9}Co_{16}B_6Nb_{0,1}$ alloy in the (a) as-cast and (b) annealed condition.

4. Conclusions

$Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ HDDR powders produced from annealed alloys yielded magnets with good remanence, energy product and squareness factor whereas a $Pr_{14}Fe_{71.9}Co_8B_6Nb_{0.1}$ alloy yielded HDDR magnets with better intrinsic coercivity. Good intrinsic coercivity was also obtained in Co-free ($Pr_{14}Fe_{80}B_6$ and $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$) HDDR magnets prepared with annealed alloys, although it had slightly reduced remanence. The best inductive coercivity was achieved when homogenized $Pr_{14}Fe_{67.9}Co_{12}B_6Nb_{0.1}$ alloy was used. These results show clearly that cobalt is essential to develop high anisotropy and SF, convenient to improve the Curie temperature and inductive coercivity but not necessary for enhancing intrinsic coercivity in Pr-based HDDR magnets.

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References

[1] T. Takeshita, R. Nakayama, in: Proceedings of the 10th International Workshop on Rare-Earth Magnets and their Applications, Kyoto, 1989, p. 551.
[2] P.J. McGuiness, X.J. Zang, X.J. Yin, I.R. Harris, J. Less-Common Met. 158 (1990) 355.
[3] S. Hirosawa, M. Uehara, S. Mino, N. Ishigaki, T. Tomida, J. Appl. Phys. 81 (8) (1997) 4821.

[4] O. Gutfleish, I.R. Harris, in: Proceedings of the 15th International Workshop on Rare-Earth Magnets and their Applications, Dresden, September, 1998, p. 487.

[5] W. Pan, L.Y. Cui, P. Wang, S. X. Zhou, in: Proceedings of the 14th International Workshop on Rare-Earth Magnets and their Applications, Sao Paulo, 1996, p. 467.

[6] Y.B. Kim, W.Y. Jeung, J. Appl. Phys. 83 (1) (1998) 6405.

[7] R.N. Faria, A.J. Williams, I.R. Harris, J. Alloys Compd. 287 (1999) L10.

[8] R.N. Faria, A.J. Williams, I.R. Harris, J. Magn. Magn. Mater 202 (1999) 349.

[9] R.N. Faria, D.N. Brown, I.R. Harris, J. Alloys Compd. 296 (2000) 219.

[10] R.N. Faria, B.E. Davies, D.N. Brown, I.R. Harris, J. Alloys Compd. 296 (2000) 223.

[11] N. Cannesan, D.N. Brown, A.J. Williams, I.R. Harris, J. Magn. Magn. Mater 233 (2001) 209.

[12] R.N. Faria, H. Takiishi, A.R.M. Castro, L.F.C.P. Lima, I. Costa, J. Magn. Magn. Mater 246 (2002) 351.

[13] J.C.S. Onelly, A.P. Tschiptschin, F.J.G. Landgraf, in: Proceedings of the Eighth International Symposium on Magnetic Anisotropy and Coercivity in Rare-Earth Transition Metal Alloys, Birmingham, September, 1994, p. 261.

[14] N. Cannesan, J.M. LeBreton, A.J. Williams, I.R. Harris, J. Magn. Magn. Mater 242–245 (2002) 1372.

[15] F.D. Saccone, C.E.R. Torres, F.H. Danchez, O. Gutfleishch, Physica B 320 (2002) 312.