

The effect of praseodymium content on the microstructure and magnetic properties of PrFeCoBNb 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 Pr-based magnets represented by the formula $\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$. Bonded magnets were prepared from cast and homogenized alloys using the hydrogenation, disproportionation, desorption and recombination process. The influence of Pr content on the magnetic properties of these magnets was studied. Praseodymium content has a significant influence on the magnetic behaviour of these magnets. Examination of the microstructures of the magnets revealed that the shape of the magnetic grains ($< 1 \mu\text{m}$) changed with praseodymium content.

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1. Introduction

The hydrogenation, disproportionation, desorption and recombination (HDDR) process has been successfully employed to produce neodymium-based bonded magnets (examples in Refs. [1–4]). In the past, magnetic $\text{Pr}_{13}\text{Fe}_{81}\text{B}_6$ powders were produced via the HDDR process, but with inferior magnetic properties, compared to substituted $(\text{Pr}_{1-x}\text{Nd}_x)_{13}\text{Fe}_{81}\text{B}_6$ materials [5]. Furthermore, the production of $\text{Pr}_{13}\text{Fe}_{55.9}\text{Co}_{24}\text{B}_6\text{Ga}_1\text{Zr}_{0.1}$ HDDR powders with good remanence was also reported, but the coercivities were still quite poor

[6]. Recently, it was shown that anisotropic powders based on the composition $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{Nb}_{0.1}$, with good remanence and coercivity ($B_r \approx \mu_0 i H_c \approx 1 \text{ T}$), can be produced by this process [7–11]. More recently, the effects of cobalt content on the magnetic properties and microstructure of $\text{Pr}_{14}\text{Fe}_{79.9-x}\text{Co}_x\text{B}_6\text{Nb}_{0.1}$ HDDR magnets have also been shown [12]. This article reports the results of further investigations carried out on $\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ -type alloys ($x = 12.0, 12.5, 13.0, 13.5, 14.0$). This study was undertaken to optimise the praseodymium content with respect to magnetic properties of HDDR permanent magnets. Cobalt- and niobium-free alloys have also been included in this study for comparison. The microstructures of the HDDR materials were observed with a scanning electron microscope (SEM).

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2. Experimental procedure

Various commercial alloys in the as-cast state and after homogenization 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 results of the microstructural examinations of the homogenized alloys are to be published elsewhere [13]. Details of the HDDR magnet preparation, heat treatments to homogenise the alloy and magnetic measurements have been described in previous papers [7–11]. Permeameter measurements were performed after saturation in a pulsed field of 6.0 T. Remanence values were normalized assuming 100% density for the HDDR sample, and by considering a linear relationship between density and remanence. The microstructural examination of the HDDR material was carried out with the aid of a scanning electron microscope (SEM).

3. Results and discussion

The variation in the remanence of the HDDR magnets, produced from as-cast and homogenized Pr-based alloys, as a function of praseodymium content is shown in Fig. 1. Good remanence values were obtained in the samples prepared from homogenized alloys containing more than 12 at% Pr. In the presence of 13.5 at% Pr, the remanence increased from 720 ± 14 to 1020 ± 20 mT. At higher praseodymium contents this property decreased. Overall, and as expected, the remanence of the

magnets produced from the alloy in the homogenized state was higher than that of magnets produced from the as-cast alloy. For the HDDR magnets produced from the $\text{Pr}_{12}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy this was not the case. This behaviour was attributed to the poorer magnetic isolation of the magnetic grains after heat treatment, mainly in alloys with a very low praseodymium content. It is appropriate to mention that even though the present HDDR treatment [7–10] was developed for alloys with a higher Pr content (13.7 at%), the procedure can be optimized to improve the magnetic properties of powders produced from alloys with a lower Pr concentration.

Fig. 2 shows the variation in the intrinsic coercivity of HDDR magnets prepared from as-cast and homogenized alloys as a function of praseodymium content. In general, better

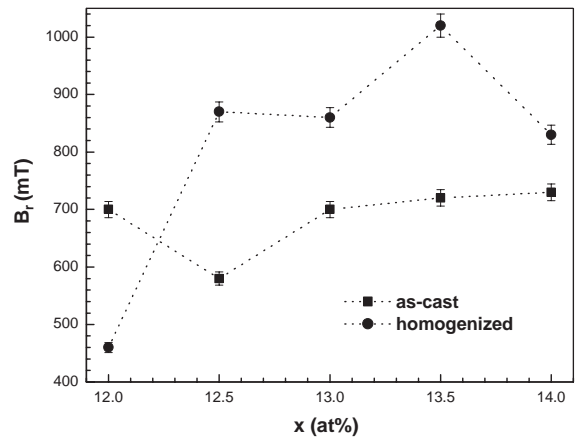


Fig. 1. Remanence versus Pr content for $\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ -type HDDR magnets.

Table 1
Composition of the as-cast alloys

Nominal composition (at%)	Analysed composition (wt%)					
	Pr	Fe	Co	B	Nb	Al
$\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	26.18	57.81	14.78	0.98	0.17	0.08
$\text{Pr}_{12.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	27.60	56.40	14.73	1.06	0.15	0.06
$\text{Pr}_{13.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	28.32	55.81	14.61	1.05	0.15	0.06
$\text{Pr}_{13.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	29.30	54.89	14.53	1.03	0.15	0.10
$\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	30.35	54.10	14.34	0.96	0.14	0.11
$\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6$	30.01	54.56	14.31	1.01	—	0.11
$\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{B}_6$	30.30	68.62	—	0.99	—	0.09

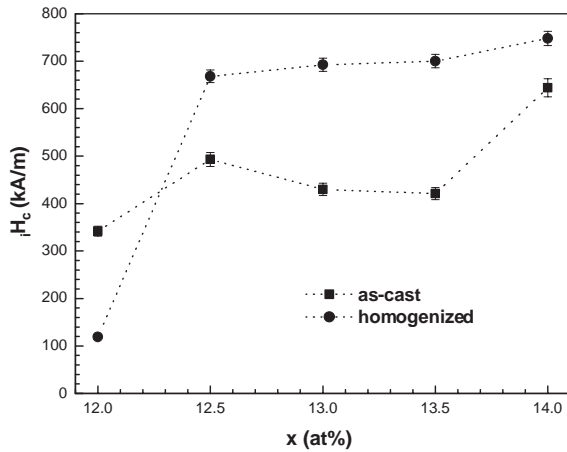


Fig. 2. Coercivity versus Pr content for $\text{Pr}_x\text{Fe}_{77.9-x}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ -type HDDR magnets.

coercivity values were obtained in specimens prepared using the homogenized alloys. The magnet with the highest coercivity (748 ± 15 kA/m) had 14 at% Pr. In this case the heat treatment of the alloy had almost no effect. Similar to the remanence behaviour of the $\text{Pr}_{12}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ magnet, the intrinsic coercivity of the HDDR magnet produced from the as-cast alloy was better. The microstructure of the HDDR material obtained from the homogenized Pr-based alloys is shown in Figs. 3–5. The grains are less rounded as the Pr content is increased to 14 at% (Fig. 5a).

The magnetic properties of all the magnets produced with alloys in the as-cast and homogenized conditions are shown in Table 2. The properties of Co- and Nb-free magnets are also

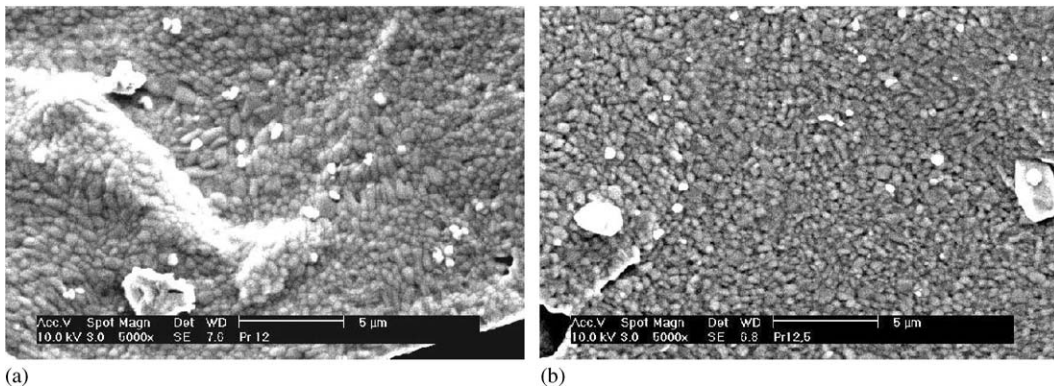


Fig. 3. Backscattered electron image of HDDR material prepared from the homogenized alloys: (a) $\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$; and (b) $\text{Pr}_{12.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$.

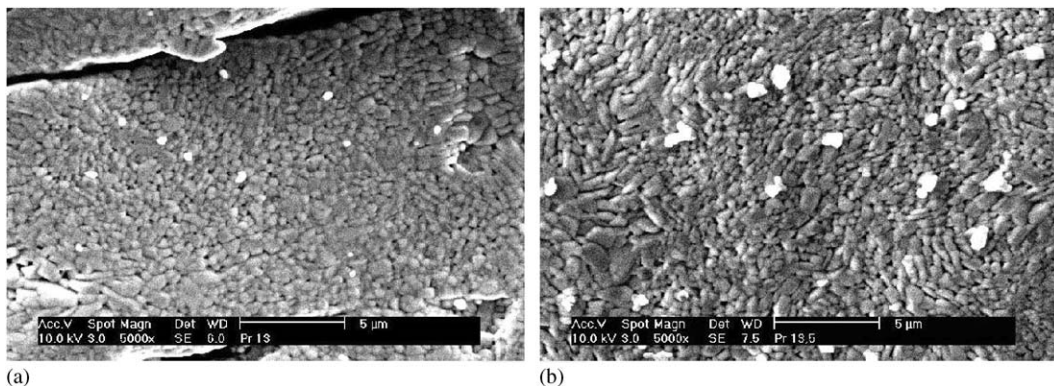


Fig. 4. Backscattered electron image of HDDR material prepared from the homogenized alloys: (a) $\text{Pr}_{13.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$; and (b) $\text{Pr}_{13.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$.

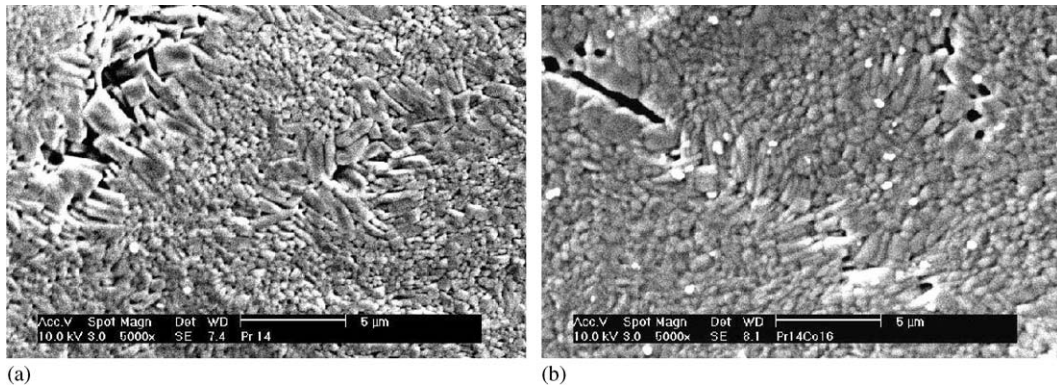


Fig. 5. Backscattered electron image of HDDR material prepared from the homogenized alloys: (a) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$; and (b) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6$.

Table 2
Magnetic properties of Pr-based HDDR magnets (error: $\pm 2\%$)

Composition	Alloy condition	B_r (mT)	iH_c (kA/m)	bH_c (kA/m)	$(\text{BH})_{\text{max}}$ (kJ/m^3)	SF (ratio)
$\text{Pr}_{12.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	As-cast	700	342	239	48	0.23
	Homogenized	460	119	95	22	0.26
$\text{Pr}_{12.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	As-cast	580	493	279	49	0.27
	Homogenized	870	668	461	119	0.40
$\text{Pr}_{13.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	As-cast	700	430	294	64	0.30
	Homogenized	860	692	477	123	0.44
$\text{Pr}_{13.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	As-cast	720	421	286	70	0.30
	Homogenized	1020	700	525	162	0.45
$\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$	As-cast	730	644	382	70	0.20
	Homogenized	830	748	477	101	0.34
$\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6$	As-cast	720	589	334	77	0.34
	Homogenized	700	748	398	80	0.32
$\text{Pr}_{14.0}\text{Fe}_{\text{bal}}\text{B}_6$	As-cast	620	748	366	59	0.28
	Homogenized	680	923	462	81	0.29

shown, for comparison. The highest energy product ($162 \pm 3 \text{ kJ/m}^3$) was observed in the magnet containing 13.5 at% praseodymium, which was prepared from a homogenized alloy. This is in agreement with data reported earlier for an alloy containing 13.7 at% Pr [7–10]. The addition of niobium increased the remanence from 610 ± 12 to 830 ± 17 mT in the HDDR magnets prepared from homogenized alloys but decreased the intrinsic coercivity from 923 ± 18 to 748 ± 15 kA/m. The highest inductive coercivity ($525 \pm 10 \text{ kA m}^{-1}$) as well as the best squareness factor ($\text{SF} = 0.45$) were also achieved in the $\text{Pr}_{13.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ magnet. The effects of niobium/cobalt additions and Pr content on the microstructure of these alloys

are shown in Figs. 6–9. A comparison of the microstructures in Figs. 6a and b reveals that the addition of cobalt refines the magnetic grains, whereas the simultaneous addition of cobalt and niobium does not cause marked changes in the microstructure (Figs. 6a and 7a). In the cobalt-containing alloy the $\text{Pr}(\text{FeCo})_2$ and $\text{Pr}_3(\text{FeCo})$ phases were observed at the grain boundaries. An increase in the Pr content of the as-cast alloys, from 12 to 14 at%, did not reveal any significant differences in their microstructures. The composition of the various phases present in the $\text{Pr}_{12}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy, both in the as-cast and homogenized conditions, are given in Table 3. These phases have also been found in other

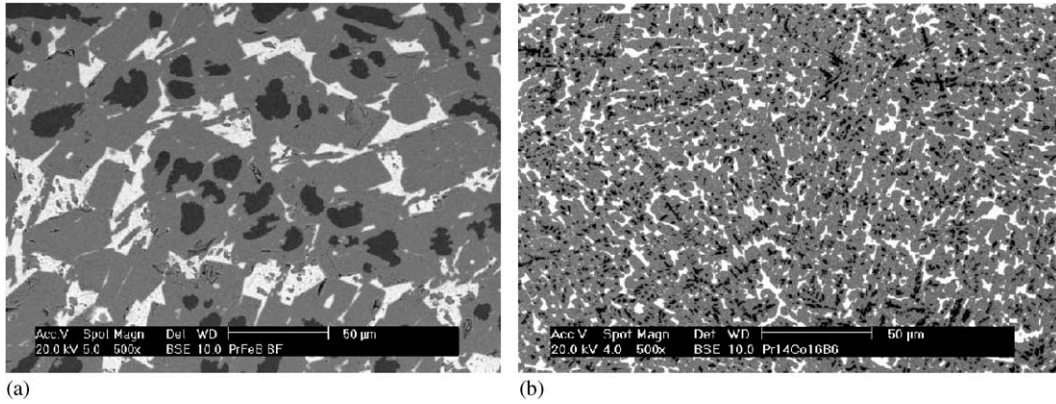


Fig. 6. Backscattered electron image of the (a) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{B}_6$ and (b) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6$ alloys in the as-cast condition.

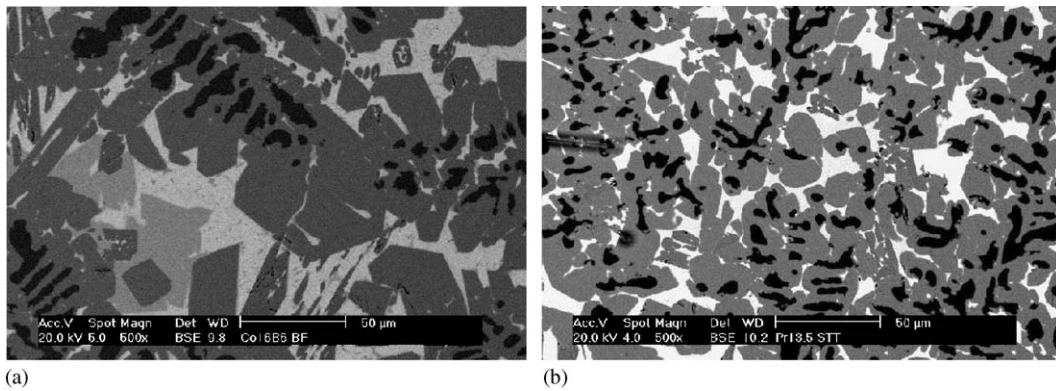


Fig. 7. Backscattered electron image of the: (a) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$; and (b) $\text{Pr}_{13.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloys in the as-cast condition.

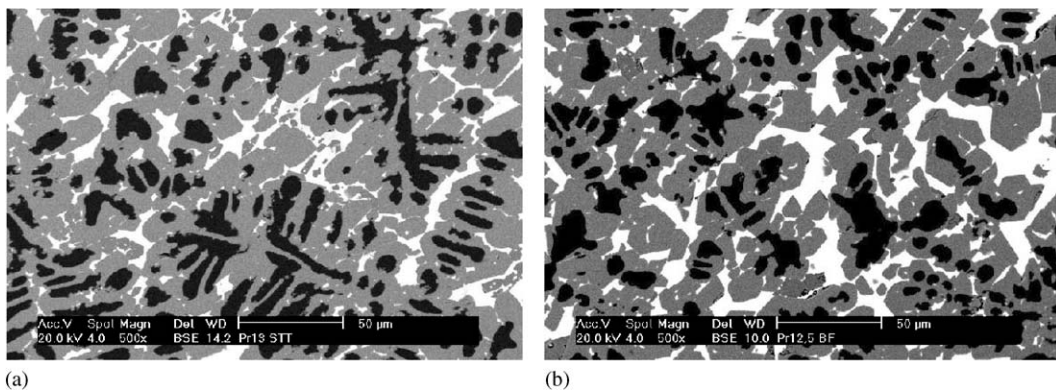


Fig. 8. Backscattered electron image of the: (a) $\text{Pr}_{13}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$; and (b) $\text{Pr}_{12.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloys in the as-cast condition.

Co-containing alloys, with the exception of the boride phase ($\text{Pr}_{1+\epsilon}\text{Fe}_4\text{B}_4$), which was only found in the alloy with 12 at% Pr. The different phases

were identified and reported earlier [12,13]. In Fig. 9b no evidence of the dark phase ($\alpha\text{-FeCo}$) was found, indicating that the homogenization

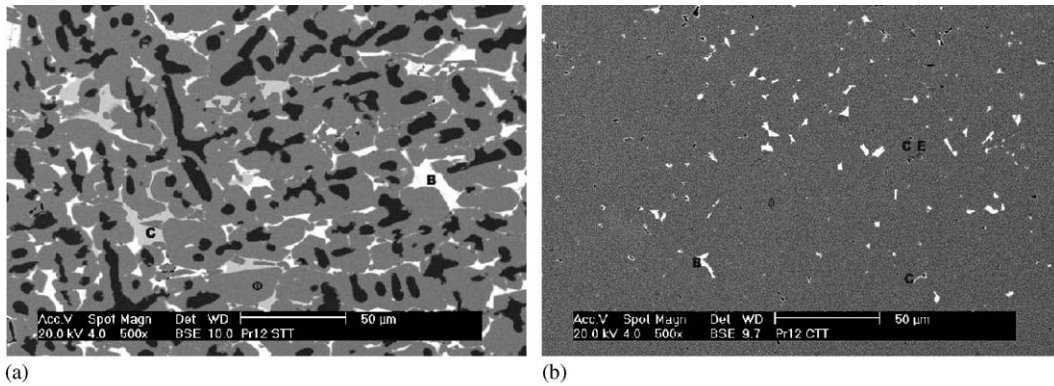


Fig. 9. Backscattered electron image of the $\text{Pr}_{12}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy in the: (a) as-cast; and (b) annealed condition.

Table 3

Composition of phases in $\text{Pr}_{12}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy, as determined by EDX

Alloy composition	Phases	Pr (at%)	Fe (at%)	Co (at%)
As-cast	$\text{Pr}_2(\text{FeCo})_{14}\text{B}$	13.4 ± 1.1	68.5 ± 0.6	18.4 ± 1.2
	$\text{Pr}(\text{FeCo})_2$	32.9 ± 0.8	24.1 ± 1.2	43.0 ± 0.9
	$\text{Pr}_3(\text{FeCo})$	66.8 ± 0.7	6.4 ± 3.4	26.8 ± 1.5
	FeCo	<1	85.6 ± 0.5	13.7 ± 1.3
Homogenized	$\text{Pr}_2(\text{FeCo})_{14}\text{B}$	12.8 ± 1.2	68.8 ± 0.6	18.4 ± 1.2
	$\text{Pr}_{1+\varepsilon}\text{Fe}_4\text{B}_4$	21.3 ± 0.9	59.0 ± 0.7	19.7 ± 1.3
	$\text{Pr}(\text{FeCo})_2$	29.4 ± 0.9	43.9 ± 0.8	26.6 ± 1.2
	$\text{Pr}_3(\text{FeCo})$	63.7 ± 0.7	97 ± 2.3	26.6 ± 1.4

heat treatment was effective even for the alloy with a very low Pr content. After this treatment the microstructures of all the Pr-based alloys are similar, and this is shown in Ref. [13].

4. Conclusions

$\text{Pr}_{13.5}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ HDDR powders produced from homogenized alloys yielded magnets with the best remanence, energy product, squareness factor and inductive coercivity. The best intrinsic coercivity was obtained in $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{B}_6$ and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{B}_6\text{Nb}_{0.1}$ HDDR magnets prepared with homogenized alloys, although with a reduced remanence. Cobalt and niobium are necessary for achieving good overall magnetic properties in praseodymium-based HDDR magnets. For the HDDR treatment used in these

experiments the Pr content in these alloys should be around 13.5 at%.

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