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Effect of boron content on magnetic properties and microstructure of PrFeCoBNb HDDR permanent magnets

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Abstract

The effect of boron content (4–8 at%) on the microstructure of Pr–Fe–Co–B–Nb alloys has been investigated using scanning electron microscopy and energy dispersive x-ray analysis. Permanent magnets were prepared from cast and annealed alloys using the hydrogenation, disproportionation, desorption and recombination process. The magnetic properties of magnets with the composition $Pr_{14}Fe_{69.9-x}Co_{16}B_xNb_{0.1}$ were assessed using a permeameter technique. It has been shown that annealing and boron content have a dramatic effect on the microstructure of the alloy and also on the magnetic behaviour of these bonded magnets.

Keywords: Pr-based alloys; Magnetic materials; Hydrides; Magnetic properties

1. Introduction

Over the past five years, extensive research has been done to study Pr–Fe–Co–B-type magnets obtained by the hydrogenation, disproportionation, desorption and recombination (HDDR) process [1–10]. Recently, it was shown that the amount of cobalt ($Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$) has a significant influence on the microstructure of magnetic alloys and on the properties of HDDR magnets [11]. More recently, it was shown that the praseodymium content ($Pr_xFe_{77.9-x}Co_{16}B_6Nb_{0.1}$) also has a great influence in Pr-based alloys and HDDR materials [12]. Similar influence has been obtained with the niobium concentration ($Pr_{14}Fe_{64-y}Co_{16}B_6Nb_y$) in these magnets [13]. This paper reports the results of further investigations carried out on $Pr_{14}Fe_{69.9-x}Co_{16}B_xNb_{0.1}$ alloys and magnets ($x = 4$–8) and was undertaken to optimize the boron content in terms of the magnetic properties of the HDDR magnets. The microstructures of the magnetic alloys, before and after annealing, were examined using scanning electron microscopy (SEM). Phase compositions were determined using an energy dispersive X-ray (EDX) spectrometer system fitted to the scanning electron microscope.

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2. Experimental procedure

Various commercial alloys in the as-cast state and after homogenisation 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). Details about the preparation of the HDDR magnets, alloy homogenisation heat treatment and magnetic measurements have been described in previous papers [1–7,11,12]. Permeameter measurements were carried out after saturation in a pulsed field of 6.0 T. Remanence values were normalized assuming 100% density for the HDDR sample, and by also considering a linear relationship between density and remanence. Microstructural characterization of the HDDR material was carried out with the aid of a SEM coupled to an EDX analysis facility.

3. Results and discussion

Variation in remanence of HDDR magnets, produced from as-cast and annealed Pr-based alloys, as a function of boron content is shown in Fig. 1. In general and as expected, the remanence of the HDDR magnets produced from the alloy in the annealed condition was higher than that of magnets produced from the as-cast alloy. Low boron content (4 and 5 at%) proved to be detrimental to this magnetic property. In the presence of 6 at% B, annealing increased the remanence from 730 to 830 mT. At higher boron contents (7 and 8 at%), the remanence decreased.

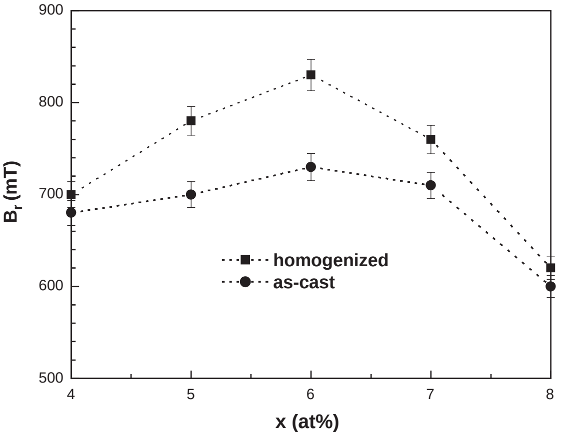

Fig. 1. Remanence versus boron content for $Pr_{14}Fe_{bal}Co_{16}B_xNb_{0.1}$-type HDDR magnets.

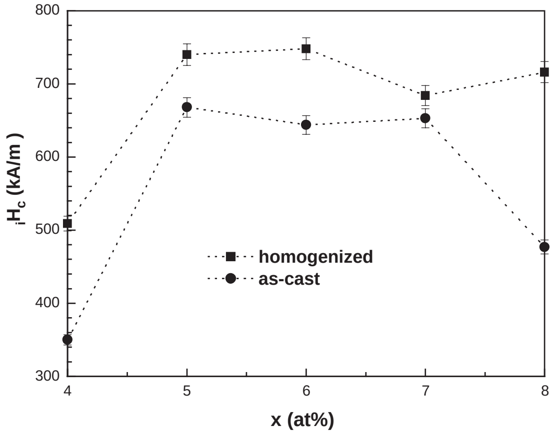

Fig. 2. Coercivity versus boron content for $Pr_{14}Fe_{bal}Co_{16}B_xNb_{0.1}$-type HDDR magnets.

Table 1
Composition of the as-cast alloys

Nominal composition (at%)	Analysed composition (wt%)					
	Pr	Fe	Co	B	Nb	Al
$Pr_{14}Fe_{65.9}Co_{16}B_4Nb_{0.1}$	29.38	55.55	14.23	0.63	0.13	0.08
$Pr_{14}Fe_{64.9}Co_{16}B_5Nb_{0.1}$	29.95	54.70	14.28	0.83	0.14	0.10
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	30.35	54.11	14.34	0.96	0.14	0.10
$Pr_{14}Fe_{62.9}Co_{16}B_7Nb_{0.1}$	30.49	53.56	14.48	1.19	0.15	0.13
$Pr_{14}Fe_{61.9}Co_{16}B_8Nb_{0.1}$	30.49	53.20	14.66	1.30	0.13	0.11

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

Composition	Alloy condition	B_r (mT)	$_iH_c$ (kA/m)	$_bH_c$ (kA/m)	$(BH)_{max}$ (kJ/m^3)	SF (ratio)
$Pr_{14}Fe_{65.9}Co_{16}B_4Nb_{0.1}$	As-cast	680	350	223	38	0.10
	Homogenised	700	509	279	51	0.13
$Pr_{14}Fe_{64.9}Co_{16}B_5Nb_{0.1}$	As-cast	700	668	334	62	0.19
	Homogenised	780	740	414	84	0.24
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	As-cast	730	644	382	70	0.20
	Homogenised	830	748	477	101	0.34
$Pr_{14}Fe_{62.9}Co_{16}B_7Nb_{0.1}$	As-cast	710	653	350	79	0.27
	Homogenised	760	684	382	80	0.23
$Pr_{14}Fe_{61.9}Co_{16}B_8Nb_{0.1}$	As-cast	600	477	255	49	0.23
	Homogenised	620	716	382	65	0.33

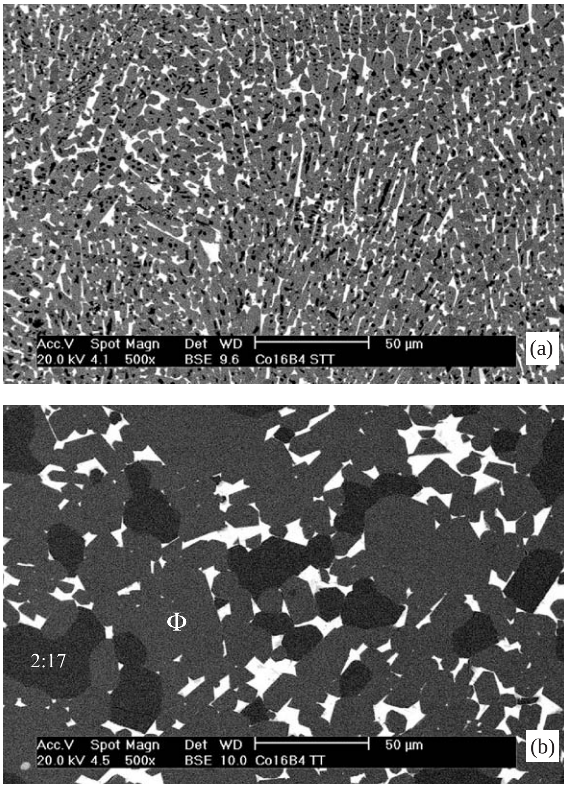

Fig. 3. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_4Nb_{0.1}$ alloy in the (a) as-cast and (b) annealed condition.

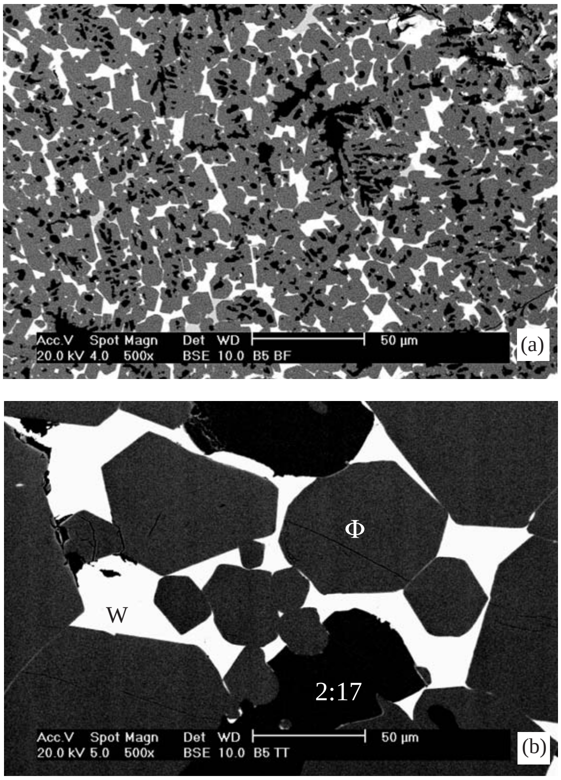

Fig. 4. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_5Nb_{0.1}$ alloy in the (a) as-cast and (b) annealed condition.

Fig. 2 shows the variation in intrinsic coercivity of HDDR magnets produced from as-cast and annealed Pr-based alloys as a function of boron content. In agreement with remanence behaviour, the coercivity of the HDDR magnets produced from the alloy in the annealed condition was higher than that of magnets produced from the as-cast alloy. Good intrinsic coercivity values

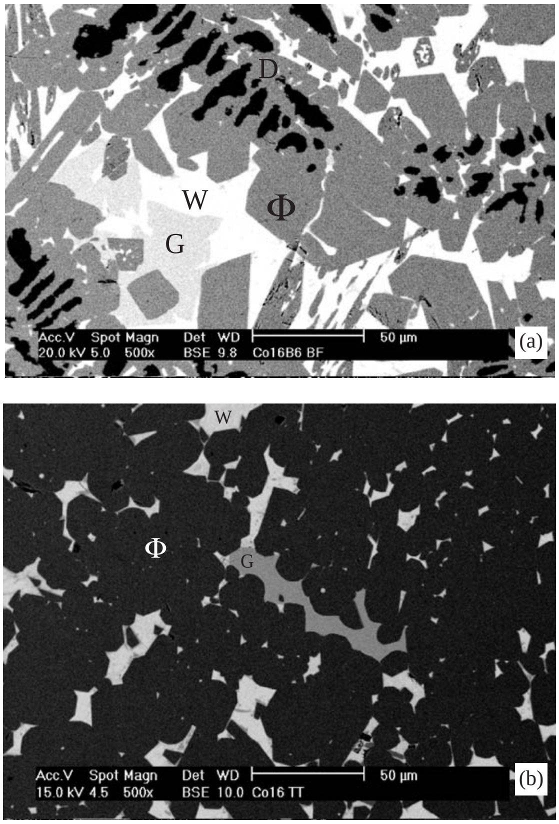

Fig. 5. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$ alloy in the (a) as-cast and (b) annealed condition. The white (W) phase is Pr_3Co and the grey (G), the Laves phase.

($\sim$740 kAm^{-1}) were achieved in samples prepared using the annealed $Pr_{14}Fe_{64.9}Co_{16}B_5Nb_{0.1}$ and $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ alloys. Low and high boron contents (4 and 8 at%) were detrimental in terms of this magnetic property.

The magnetic properties of all the magnets produced with Pr-based alloys in the as-cast and annealed conditions are shown in Table 2. The best energy product (101 kJ/m^3) was observed in the magnet containing 6 at% boron, which was prepared from an annealed alloy. The highest inductive coercivity was achieved in this HDDR magnet (477 kAm^{-1}). The best squareness factor (SF = 0.34) was also achieved in the $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ magnet.

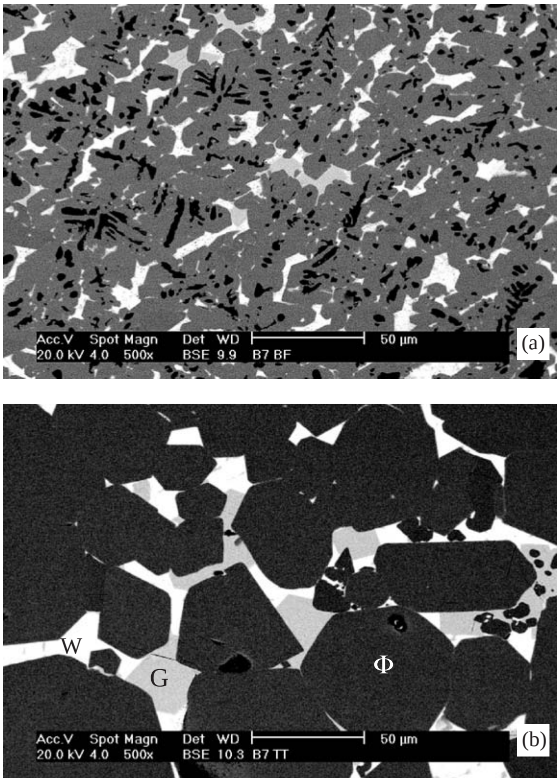

Fig. 6. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_7Nb_{0.1}$ alloy in the (a) as-cast and (b) annealed ion.

The effects of boron concentration on the microstructure of the Pr-based alloys, before and after annealing, are shown in Figs. 3–7. A Fe–Co phase is present in all alloys in the as-cast state (dark dendritic phase inside the matrix phase or Φ). This magnetically soft phase is well-known to be detrimental to the magnetic properties and most certainly is the cause of the reduced remanence and coercivity of the HDDR magnet prepared with the as-cast alloys. Comparison of the microstructures of the as-cast alloys shows that the size of the matrix grains increases with increasing boron content. The Fe–Co phase is completely eliminated upon annealing at 1100 °C for 20 h (reason of the improvement in the magnetic properties). The $Pr_{14}Fe_{65.9}Co_{16}B_4Nb_{0.1}$ and $Pr_{14}Fe_{64.9}Co_{16}B_5Nb_{0.1}$ alloys show substantial grain growth after annealing and the presence of a Pr_2Fe_{17} phase (this phase is slightly darker than the matrix phase but is not as dark as the free iron found in the as-cast alloys). This phase is also magnetically soft and detrimental to the magnetic properties of permanent magnets (by dilution of the matrix phase and nucleation of reverse domains). The 2:17 phase is not seen in the alloys with higher boron content. Two other phases (white and grey) were also found in the alloys containing 16 at% Co (see Fig. 5 for phase identification) and were identified previously [11,12] as Pr_3Co and $Pr(Fe,Co)_2$ (Laves phase).

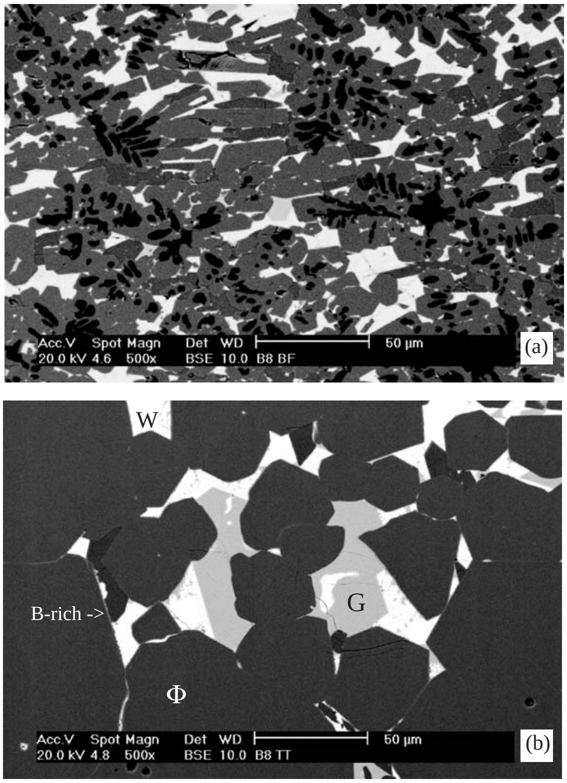

Fig. 7. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_8Nb_{0.1}$ alloy in the (a) as-cast and (b) annealed condition.

A B-rich or boride phase ($Pr_{1+\varepsilon}Fe_4B_4$) has been detected in the Pr-based alloys with 7 and 8 at% B. The paramagnetic 1:4:4-type phase has been reported to degrade the intrinsic coercivity in Nd–Fe–B-based magnets through the generation of demagnetising stray fields, which can facilitate the nucleation of reverse domains [14]. In the present study, this phase only has a detrimental effect on B_r and not on $_iH_c$ in the annealed HDDR samples. Any other phase present (rare earth-rich, B-rich, Pr_2Fe_{17}, $Pr_{1+\varepsilon}Fe_4B_4$, Laves, etc.) in the magnet besides the matrix phase ($Pr_2Fe_{14}B$) will have a diluting effect with the consequent diminution in Br and this is in agreement with the present observations. Chemical analyses of the phases are given in Table 3.

4. Conclusions

Good magnetic properties were obtained in the HDDR magnet prepared from an annealed $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ alloy. Boron contents, both above and below 6 at% decreased the magnetic properties of the HDDR permanent magnets. This result shows clearly that the optimum amount of

Table 3
Compositions determined by EDX in the various phases found in the Pr-based alloys, before and after annealing (error bars = ±2 standard deviation)

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
	FeCo	D	<1	87.2 ± 0.4	11.9 ± 1.3
	$Pr_{1+\varepsilon}(FeCo)_4B_4$	B-rich	21.1 ± 0.7	60.1 ± 0.5	18.8 ± 0.8
Annealed	$Pr_2(FeCo)_{14}B$	Φ	12.3 ± 0.6	70.1 ± 0.5	17.6 ± 0.9
	$Pr(FeCo)_2$	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
	$Pr_2(FeCo)_{17}$	2:17	11.0 ± 0.7	71.3 ± 0.5	17.7 ± 0.7
	$Pr_{1+e}(FeCo)_4B_4$	B-rich	21.8 ± 0.7	60.4 ± 0.6	17.8 ± 0.8

boron for the cobalt containing praseodymium-based HDDR magnets is 6 at%. Annealing is necessary to develop excellent magnetic properties in these HDDR magnets. Various phases were found in the cobalt-containing Pr-based magnetic alloys. These phases changed or disappeared upon annealing and with boron concentration. The phases also affected considerably the magnetic properties of the HDDR magnets.

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