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The effect of niobium content on the magnetic properties and microstructures of PrFECoBNb HDDR magnets and alloys

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Abstract

Praseodymium-based permanent magnets were prepared from cast and annealed alloys using the hydrogenation, disproportionation, desorption and recombination process. The effect of niobium content on the magnetic properties of these bonded magnets was investigated. Niobium has a significant effect on the magnetic behaviour of these hydrogen-processed materials. Best overall magnetic properties were obtained in a $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ magnet.

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

1. Introduction

Additions of niobium and zirconium are necessary to develop optimum anisotropic magnetic properties in praseodymium-based magnets produced by the hydrogenation, disproportionation, desorption and recombination (HDDR) process [1–11]. Powders based on the composition $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ can be produced with good remanence ($B_r \sim 1\,T$) and reasonable intrinsic coercivity (${}_iH_c \sim 0.8\,MA\,m^{-1}$) [3]. The amount of niobium (0.1%) in this magnet is extremely low, there being only one Nb atom in every thousand atoms of the alloy. Considering that there are 68 atoms per unit cell in the $Pr_2Fe_{14}B$ compound [12] and disregarding the presence of cobalt, this amount to roughly one atom of niobium for every 15 unit cells. Nevertheless, niobium additions induce considerable anisotropy in the PrFeCoB-HDDR magnets. The remanence of a $Pr_{13.8}Fe_{63.5}Co_{16.7}B_6$ HDDR magnet was only 869 mT, where as that of a $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Nb_{0.1}$ magnet was 1032 mT [3], indicating that remanence increased by approximately 19%

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with the addition of 0.1 at% Nb to the magnetic alloy. Optimization of the niobium content with respect to magnetic properties of cobalt-containing Pr-based HDDR magnets has not been reported so far. This paper addresses this aspect and reports the results of further work carried out on $Pr_{14}Fe_{bal}Co_{16}B_6Nb_x$-type alloys and HDDR magnets ($x = 0$, 0.01, 0.05, 0.10, 0.15, 0.50). Two Co-free Pr-based alloys ($Pr_{14}Fe_{80}B_6$ and $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$) have been included in this study for comparison. 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 dispersive X-ray (EDX) spectrometer system coupled to the SEM.

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). Details of HDDR magnet production, heat treatments to homogenize the alloy and magnetic measurements have been described in previous papers [1–7]. 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. Microstructural characterization of the HDDR material was carried out with the aid of a SEM.

3. Results and discussion

The variation in remanence and intrinsic coercivity of the permanent magnets produced from the annealed Pr-based alloys, as a function of niobium content, is shown in Fig. 1. The remanence and coercivity of the Nb-free $Pr_{14}Fe_{64}Co_{16}B_6$ HDDR magnet were 700 ± 14 mT and 748 ± 15 kA m^{-1}, respectively. In the presence of only 0.01 at% Nb, the remanence decreased from 700 ± 14 to 620 ± 12 mT. Higher Nb contents

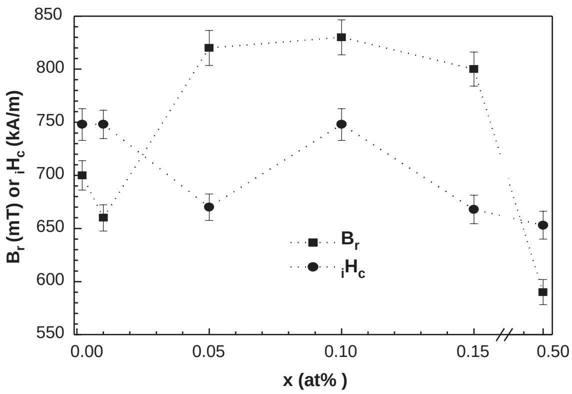


Fig. 1. Remanence and intrinsic coercivity versus Nb content for $Pr_{14}Fe_{bal}Co_{16}B_6Nb_x$-type HDDR magnets produced from homogenized alloys.

Table 1
Composition of the as-cast alloys

Nominal composition (at%)	Analysed composition (wt%)					
	Pr	Fe	Co	B	Nb	Al
$Pr_{14}Fe_{80}B_6$	30.30	68.62	—	0.99	—	0.09
$Pr_{14}Fe_{79.9}B_6Nb_{0.10}$	30.11	68.68	—	0.97	0.14	0.10
$Pr_{14}Fe_{64}Co_{16}B_6$	30.01	54.56	14.31	1.01	—	0.11
$Pr_{14}Fe_{63.99}Co_{16}B_6Nb_{0.01}$	30.21	54.27	14.39	1.00	0.02	0.11
$Pr_{14}Fe_{63.95}Co_{16}B_6Nb_{0.05}$	30.13	54.26	14.40	1.01	0.09	0.11
$Pr_{14}Fe_{63.90}Co_{16}B_6Nb_{0.10}$	30.35	54.11	14.34	0.96	0.14	0.10
$Pr_{14}Fe_{63.85}Co_{16}B_6Nb_{0.15}$	30.34	54.01	14.27	1.01	0.23	0.14
$Pr_{14}Fe_{63.50}Co_{16}B_6Nb_{0.50}$	29.79	54.09	14.40	0.96	0.67	0.09

increased this magnetic property, reaching a maximum of 830 ± 17 mT with 0.1 at% Nb. Niobium additions up to 0.05 at% decreased considerably the intrinsic coercivity of the HDDR magnets. A modest peak in ${}_iH_c$ ($748 \pm 15\,kA\,m^{-1}$) was observed in the Pr-based magnet containing 0.1 at% Nb, and this is only recovery to the initial value of intrinsic coercivity shown by the Nb-free magnet. Thus, only the addition of 0.1 at% Nb to the Pr-Fe-Co-B alloy brings about an effective improvement, i.e., inducement of anisotropy in the HDDR magnets with consequent increase in

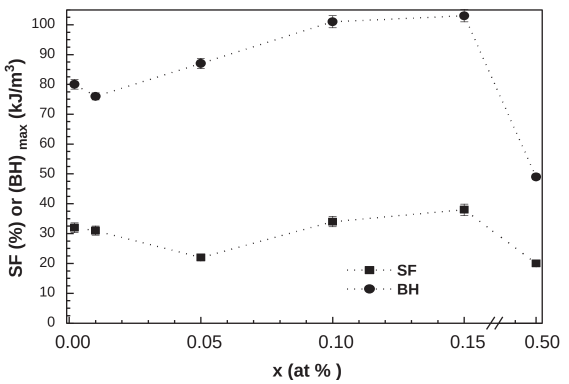


Fig. 2. Energy product and SF versus Nb content for $Pr_{14}Fe_{bal}Co_{16}B_6Nb_x$-type HDDR magnets produced from homogenized alloys.

remanence. The remanence of the $Pr_{14}Fe_{63.90}$-$Co_{16}B_6Nb_{0.10}$ magnet (830 ± 17 mT), observed in the present work, is lower than that reported in Ref. [3] (1032 ± 20 mT), and this can be attributed to differences in alloy purity and preparation conditions. The change in energy product and squareness factor (SF) of the HDDR magnets produced from the annealed Pr-based alloys, as a function of niobium content, is shown in Fig. 2. Best properties were observed in the HDDR magnets prepared from the homogenized alloy containing 0.15 at% Nb. Coincidently, the alloy used to prepare this magnet had the highest aluminium content (0.14 wt%).

The magnetic properties of all the magnets produced with alloys in the as-cast and annealed conditions are shown in Table 2. The best intrinsic coercivity ($923 \pm 18\,kA\,m^{-1}$) was observed in the magnets without cobalt, which were prepared from annealed alloys. The Co-free magnet containing 0.1 at% Nb showed the best energy product ($114 \pm 2\,kJ\,m^{-3}$). The $Pr_{14}Fe_{63.9}$-$Co_{16}B_6Nb_{0.1}$ and $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ HDDR magnets showed the highest inductive coercivity ($477 \pm 10\,kA\,m^{-1}$). The best SF ($= 0.39 \pm 0.01$) was also achieved in the latter magnet. The $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ HDDR magnet also showed a reasonable SF (0.34). The addition of 0.5 at% Nb proved to be detrimental to all

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

Composition	Alloy condition	B_r (mT)	${}_iH_c$ ($kA\,m^{-1}$)	${}_bH_c$ ($kA\,m^{-1}$)	$(BH)_{max}$ ($kJ\,m^{-3}$)	SF (ratio)
$Pr_{14}Fe_{80}B_6$	As-cast	620	748	366	59	0.28
	Homogenized	680	923	462	81	0.29
$Pr_{14}Fe_{79.9}B_6Nb_{0.10}$	As-cast	620	653	382	60	0.32
	Homogenized	790	923	477	114	0.39
$Pr_{14}Fe_{64}Co_{16}B_6$	As-cast	720	589	334	77	0.34
	Homogenized	700	748	398	80	0.32
$Pr_{14}Fe_{63.99}Co_{16}B_6Nb_{0.01}$	As-cast	720	589	334	66	0.23
	Homogenized	660	748	398	76	0.31
$Pr_{14}Fe_{63.95}Co_{16}B_6Nb_{0.05}$	As-cast	620	525	294	61	0.27
	Homogenized	820	670	382	87	0.22
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.10}$	As-cast	730	644	382	70	0.20
	Homogenized	830	748	477	101	0.34
$Pr_{14}Fe_{63.85}Co_{16}B_6Nb_{0.15}$	As-cast	600	541	310	54	0.29
	Homogenized	800	668	430	103	0.38
$Pr_{14}Fe_{63.50}Co_{16}B_6Nb_{0.50}$	As-cast	580	446	263	41	0.21
	Homogenized	590	653	302	49	0.20

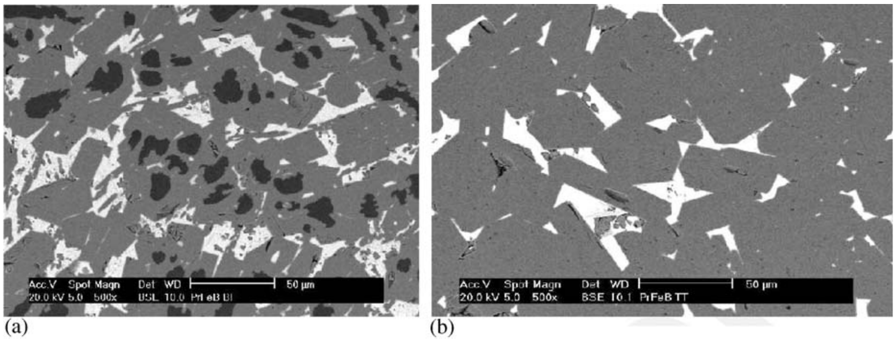


Fig. 3. Backscattered electron image of the $Pr_{14}Fe_{bal}B_6$ alloy in the (a) as-cast and (b) homogenized condition.

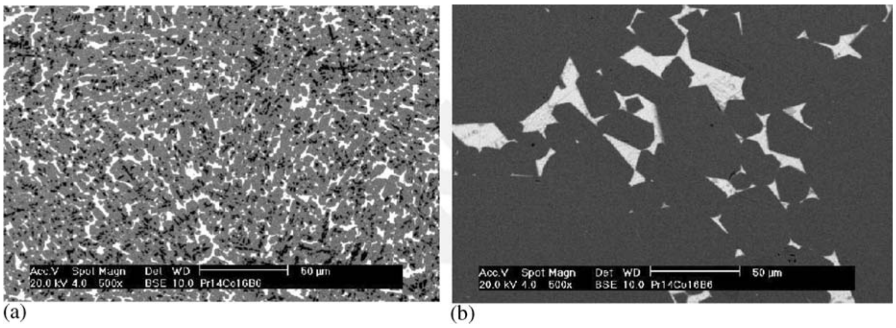


Fig. 4. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_6$ alloy in the (a) as-cast and (b) homogenized condition.

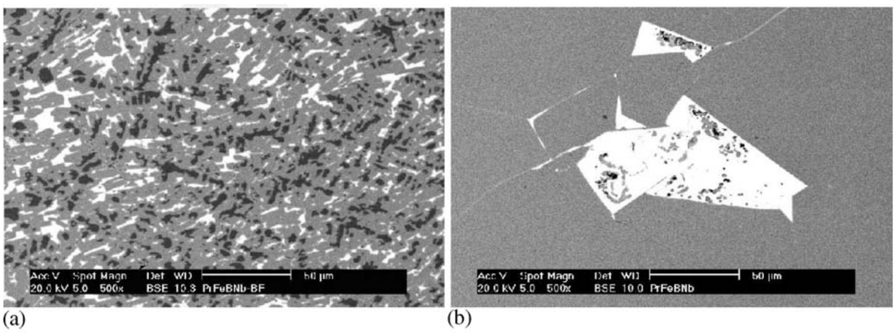
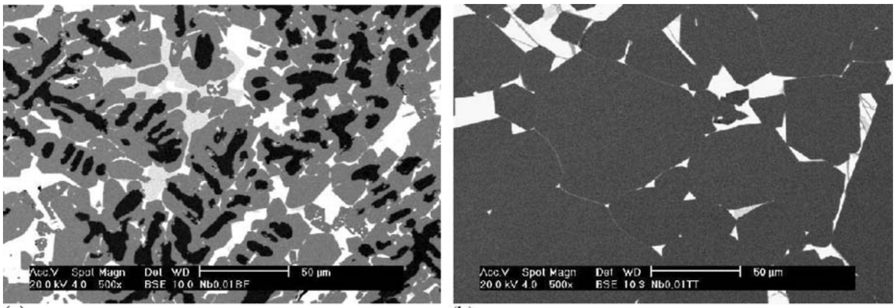


Fig. 5. Backscattered electron image of the $Pr_{14}Fe_{bal}B_6Nb_{0.1}$ alloy in the (a) as-cast and (b) homogenized condition.

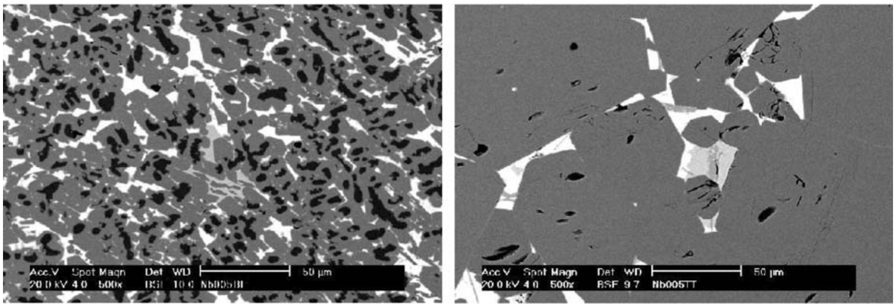
magnetic properties of the Pr-based HDDR magnets.

The effects of niobium addition on the microstructure of these alloys, before and after homogenization, are shown in Figs. 3–10. After the heat treatment at 1100°C for 20 h, grain growth is evident in all alloys (less pronounced in Fig. 8b). A comparison of the microstructures in Figs. 3a, 4a and 5a reveals that the addition of 16 at% Co or 0.1 at% Nb decreased considerably the grain size of the cast alloy. Simultaneous additions of 16 at% Co and 0.01 at% Nb resulted in



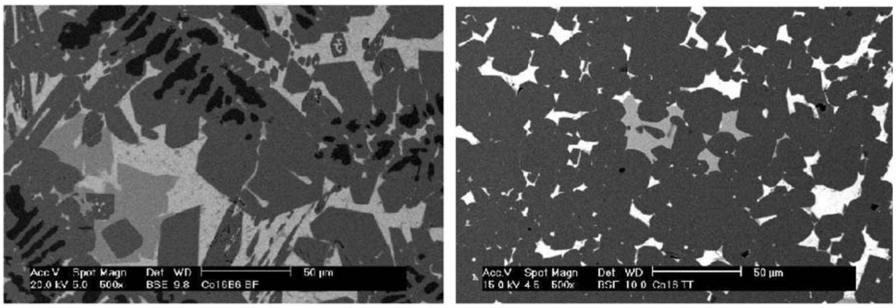
(a) (b)

Fig. 6. Backscattered electron image of the $Pr_{14}Fe_{bal}B_6Nb_{0.01}$ alloy in the (a) as-cast and (b) homogenized condition.



(a) (b)

Fig. 7. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.05}$ alloy in the (a) as-cast and (b) homogenized condition.



(a) (b)

Fig. 8. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$ alloy in the (a) as-cast and (b) homogenized condition.

matrix phase grains similar to that in the $Pr_{14}Fe_{bal}B_6$ alloy (Figs. 3a and 6a). Quite surprisingly, Nb additions to the cobalt-containing as-cast alloys yielded $Pr_2Fe_{14}B$ grains similar in size to that obtained in the Co/Nb-free alloy. Small amounts of a Nb-containing phase (54 wt% Nb, 3 wt% Pr, 35 wt% Fe and 8 wt% Co) were found at the grain boundaries of the cast $Pr_{14}Fe_{bal}$-$Co_{16}B_6Nb_{0.5}$ alloy.

4. Conclusions

Good overall magnetic properties ($B_r = 830 \pm 17\,\text{mT}$, ${}_iH_c = 748 \pm 15\,\text{kA m}^{-1}$, $(BH)_{max} =$

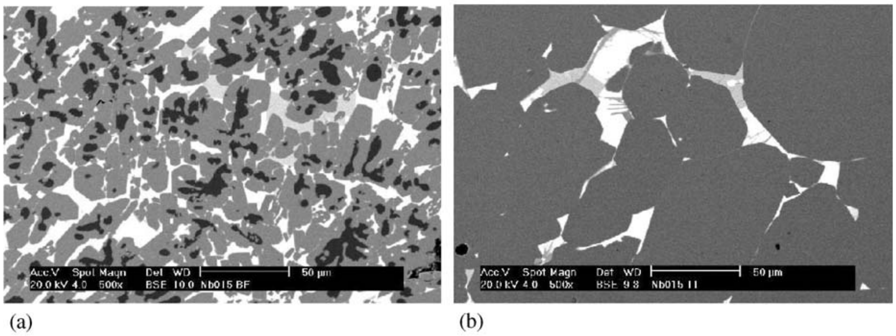


Fig. 9. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.15}$ alloy in the (a) as-cast and (b) homogenized condition.

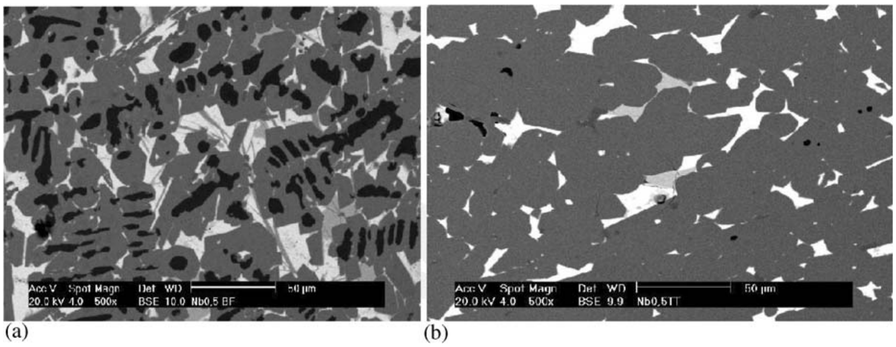


Fig. 10. Backscattered electron image of the $Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.5}$ alloy in the (a) as-cast and (b) homogenized condition.

$101 \pm 2\,kJ\,m^{-3}$ and $SF = 0.34 \pm 0.01$) have been achieved in the HDDR magnet prepared from an annealed $Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$ alloy. Best coercivity ($923 \pm 18\,kA\,m^{-1}$) was obtained in the $Pr_{14}Fe_{80}B_6$ and $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ HDDR magnets. Good intrinsic coercivity was obtained in the HDDR magnets prepared with the annealed $Pr_{14}Fe_{64}Co_{16}B_6$ alloy, although it had slightly reduced remanence. The best inductive coercivity was achieved in the homogenized alloy containing only 0.01 at% Nb. These results show that 0.1 at% of niobium is essential to develop good anisotropy and SF. Even though niobium addition improves inductive coercivity, it is not beneficial in terms of intrinsic coercivity in Pr-based HDDR magnets.

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