The effect of processing parameters on the magnetic properties of Pr-Fe-B-Cu magnets prepared using the hydrogen decrepitation and powder metallurgy route

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Abstract: Sintered permanent magnets based on the composition $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ have been prepared using the hydrogen decrepitation (HD) process and the powder metallurgy route. For particular processing conditions, annealing the sintered magnets at 1000°C, resulted in an increase in iHc from 11 to around 20 kOe. The as-cast ingot microstructure of the alloy $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ has also been modified by an homogenization heat treatment at 1000°C for 24 hours. Sintered magnets prepared using the hydrogen decrepitation process from the homogenized alloy exhibit superior remanence and energy product to those prepared from the as-cast ingot. Homogenization also showed that the influence of the initial microstructure on the intrinsic coercivity of Pr-Fe-B-Cu HD sintered permanent magnets is a minimum when the coercivity reaches the maximum value of ~20 kOe. Magnets of various standard compositions have also been investigated. The possibility of changing the easy direction of magnetization from the tetragonal c-axis to easy basal plane during hydrogen absorption has also been investigated as a means of producing radially anisotropic permanent magnets using the isostatic pressing method.

1. INTRODUCTION

For many years, hydrogen decrepitation has been employed in the processing and characterization of Nd-Fe-B-type magnets [1]. Recently great interest has arisen in Pr-Fe-B magnets due to the absence of a spin reorientation at lower temperatures when compared with Nd-Fe-B magnets [2] and hence better magnetic characteristics at low temperatures. The addition of elements such as Cu, Ag, Au or Pd has led to alloys with good magnetic properties in the form of hot-pressed and hot-rolled magnets [3-5]. Very recently, the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy has been found to exhibits iHc values of 10-12 KOe in the cast ingots after annealing [6]. It has also been reported [7, 8] that $Pr_2Fe_{14}B$ when in the hydride form changes its easy direction of magnetization from the tetragonal c-axis to easy basal plane which, in practice, could produce radially anisotropic magnets. An initial heat treatment for homogenization, usually at elevated temperature and for a few days, has been applied to Nd-Fe-B and Pr-Fe-B-Cu alloys [6, 9] to eliminate free iron and composition gradients, by accelerating the solid-state diffusion and consequently yielding a more homogeneous alloy. In the present work, sintered magnets of compositions $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$, $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$, $Pr_{16}Fe_{76}B_8$ and $Pr_{16.9}Fe_{79.1}B_4$ have been prepared via the HD process and in view of the changes observed in the hot pressed ingots [3] the effect of annealing on their coercivity has been studied. The possibility of producing radially aligned magnets and the ingot homogenization heat treatment and milling time influencing the final magnetic properties of HD sintered magnets of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy has also been investigated.

2. EXPERIMENTAL

The alloys investigated in this study have been provided by Rare Earth Products Ltd. In order to produce the magnets via the HD process [1], the following procedure was adopted. Small pieces of the bulk ingot were placed in a stainless steel hydrogenation vessel which was evacuated to backing-pump pressure and hydrogen was then introduced to a pressure of 10 bar. The decrepitated material was then transferred to a "roller" ball-mill under a protective nitrogen atmosphere and milled using cyclohexane as the milling medium. The resultant fine powder was then dried and transferred into in a small cylindrical rubber tube, pulsed in a magnetic field of 6 T and isostatically pressed. The consequent green compacts were then vacuum sintered at 1060°C for 1 hour and furnace cooled. The as-sintered magnets then received a post sintering heat treatment [3] under vacuum at 1000 °C for 24 hours and their magnetic properties were determined in a permeameter. The homogenization heat treatment of the ingot was carried out under vacuum at 1000°C for 24 hours and slow cooled in the furnace (cooling rate of approximately 3.5°C/min). The heat treated ingot (homogenized) was then processed in the same manner as the bulk ingot.

3. RESULTS AND DISCUSSION

3.1 The Effect of Milling Time and Annealing on iHc

The effects of milling time and annealing at 1000°C for 24 hours are shown in Fig.1a. The most striking feature of this graph is the variation of intrinsic coercivity with the milling time for the annealed samples. The $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnet exhibits a remarkable increase in iHc in the powder milled for 9 hours. Another distinct feature is that, even for as-crushed material with a coarse particle size (zero milling time in Fig.1a), the magnet exhibits appreciable coercivity. The demagnetization curves of the magnets prepared with powder milled for 9 hours are shown in fig. 1b.

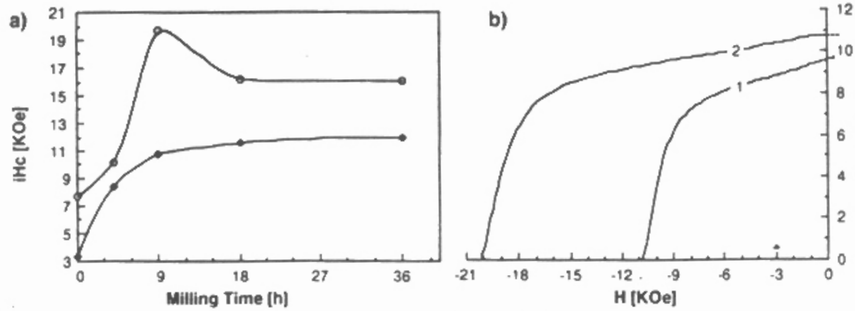

Fig. 1 (a) Variation of iHc with the milling time for slow cooled magnets of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy (◊:As-sintered, o : annealed 1000°C,24 hours) and (b) the demagnetization curves for slow cooled magnets prepared with powder milled for 9 hours, before (curve 1) and after annealing (curve 2).

Microstructural investigations [10] have shown that the increase in the coercivity of $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD sintered magnets with a high temperature heat treatment can be attributed partially to the better magnetic isolation of the $Pr_2Fe_{14}B$ grains obtained with this treatment. It was also reported [10] that the amount of a Pr_2Fe_{17} phase, found in the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnets, decreased after the post sintering heat treatment and this could also be responsible for the enhanced coercivity in this magnet. In addition, in the as-sintered condition the Pr_2Fe_{17} phase was closely associated with the matrix phase whereas after annealing it occurred as individual isolated grains. A $Pr_{34}Fe_{62}Cu_4$ phase was also identified in a magnet annealed at 1000°C for 24 hours but the similar coercivity behaviour of a Cu-free, $Pr_{16.9}Fe_{79.1}B_4$ magnet on annealing at 1000°C indicated that the presence of such a phase may only have resulted in a small additional improvement in the coercivity.

3.2 The effect of ingot heat treatment on the magnetic properties of the HD sintered magnets

The magnetic properties of $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnets prepared from the homogenized alloy compared with those prepared from the standard as-cast ingot alloy are shown in Table1. The percentage change in the magnetic properties achieved by the homogenization treatment, which summarizes the magnetic behaviour, is also given in Table 1. Microstructural changes with homogenization are reported in Ref. 6.

Table 1 Magnetic properties and percentage variation in the magnetic properties of $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnets prepared from as-cast and homogenized alloy (*homogenized value)

Milling time	Property and Variation (%)								
	$(BH)_{max}^*$	$(BH)_{max}$	$\Delta(BH)_{max}$	B_r^*	B_r	Δ Br	iH_c^*	iH_c	Δ iHc
Crushed	11.0	4.9	124.5	7.8	4.9	59.2	6.4	7.7	-16.9
4 h	27.6	22.7	21.6	10.9	10.0	9.0	9.1	10.2	-10.8
9 h	25.4	24.9	2.0	10.1	10.7	-5.6	20.2	19.7	2.5

(The percentage variation equation is $\Delta x(\%)=[(x^*/x)-1]100$, where x^* is the value for the homogenized material. A positive value of Δx corresponds to an increase in the magnetic property with the homogenization heat treatment, and a negative value corresponds to a decrease. Average error: Br : ± 0.1KG, iHc : ± 0.5KOe, (BH)max : ± 0.9 MGOe)

The largest influence of the initial state of the ingot material is observed for the magnets prepared using the alloy in the crushed state, where a very appreciable increase in energy product and remanence occurred with homogenization. However, this influence became less significant with progressive milling time and the percentage change in energy product, remanence and intrisic coercivity becomes very small around 9 hours of milling time. Thus the present observations on the alloy $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ indicates that a rehomogenization of the initial cast material occurs as a result of the progressive milling and subsequent sintering and annealing treatment. This can be ascribed to the progressively finer particle size of the green compacts which then results in more rapid diffusion during liquid phase sintering and subsequent post sintering heat treatment. This results in the progressive diminution in the influence of the initial cast structure and phase distribution on the magnetic properties of the sintered magnets.

3.3 The Effect of Annealing on the Magnetic Properties of Magnets of Various Compositions

The optimum milling time and magnetic properties (before and after annealing) of HD sintered magnets of various compositions are given in Table 2. The $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ HD magnet also exhibits some enhancement in iHc after annealing but at a longer milling time (18 hours). The demagnetisation curve for this magnet is shown in fig. 2 (a). Lower coercivity has been found with these magnets but a higher remanence and energy products have been achieved.

Table 2 Comparison of various HD sintered permanent magnets .

ALLOY TYPE		Milling time[h]	Br [kG]	iHc [kOe]	bHc [kOe]	(BH)max [MGOe]	S.F ratio	ρ g / cm³
$Pr_{20.5}Fe_{73.8}B_{3.7}Cu$	As-sintered	09	9.6	10.8	7.6	18.5	0.38	7.3
	Annealed		10.7	19.8	9.5	24.9	0.39	7.3
$Pr_{17}Fe_{76.5}B_5Cu_{1.5}$	As-sintered	18	10.4	6.4	5.4	22.1	0.64	7.3
	Annealed		11.1	12.4	8.5	29.0	0.60	7.3
$Pr_{16}Fe_{76}B_8$	As-sintered	18	10.8	14.9	10.2	29.3	0.77	7.3
	Annealed		10.9	17.5	10.5	29.2	0.81	7.3
$Pr_{16.9}Fe_{79.1}B_4$	As-sintered	27	10.3	11.7	8.8	22.9	0.51	7.1
	Annealed		10.6	20.3	9.6	25.3	0.49	7.1
$Pr_{16}Fe_{76}B_8$	As-sintered	45	11.4	13.9	10.6	31.2	0.84	7.3
	Annealed		11.5	14.9	11.1	32.1	0.93	7.3

The $Pr_{16.9}Fe_{79.1}B_4$ HD magnet also exhibits a dramatic enhancement in iHc after annealing but at a significantly longer milling time (27 hours). Demagnetization curves for the as-sintered and annealed magnets (24 hours, 1000°C) are shown in the fig. 2 (b). The $Pr_{16.9}Fe_{79.1}B_4$ magnet exhibits a slightly superior squareness factor (loop shape) than the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet, before and after annealing.

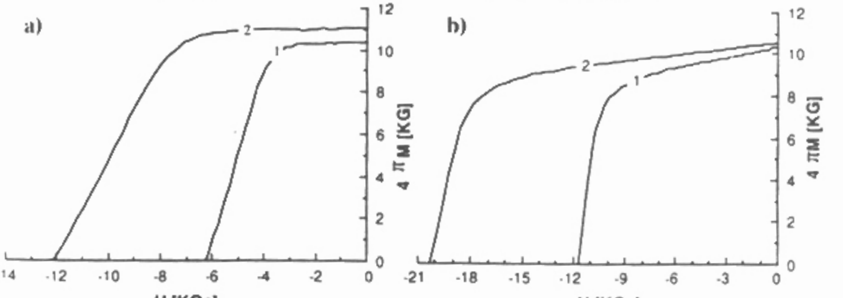

Fig.2 The demagnetization curves for slow cooled magnets of the (a) $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ and (b) $Pr_{16.9}Fe_{79.1}B_4$ alloys, before (curve 1) and after annealing (curve 2).

Two optimum milling time have been found for the $Pr_{16}Fe_{76}B_8$ magnets. The demagnetization curves for slow cooled magnets of the $Pr_{16}Fe_{76}B_8$ alloy milled for 18 hours and 45 hours are shown in fig. 3 (a) and (b), respectively. The former exhibits a superior intrinsic coercivity whereas the remanence and energy product in the latter are significantly higher. A very square demagnetization loop (squareness factor: SF=0.93) is obtained when the milling time is 45 hours, as shown in fig. 3 (b). The intrinsic coercivity obtained in the $Pr_{16}Fe_{76}B_8$ magnets is lower than that of $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD sintered magnets, however the $Pr_{16}Fe_{76}B_8$ HD magnets exhibit higher Br, $(BH)_{max}$ and squareness factor. Similar coercivities have also been obtained in annealed $\ldots Fe_{80}B_5$ magnets produced by mechanical grinding [11].

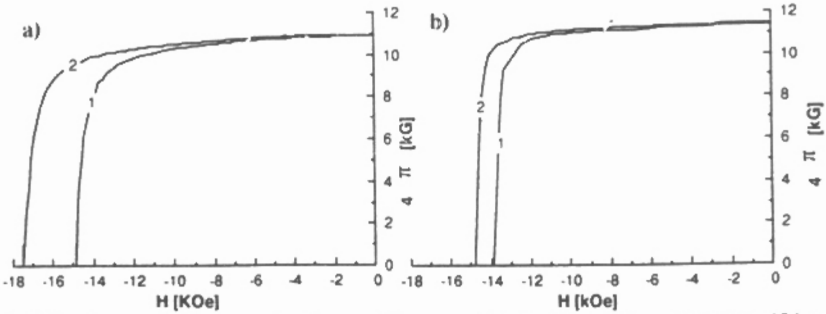

Fig. 3 The demagnetization curves for slow cooled magnets of the $Pr_{16}Fe_{76}B_8$ alloy milled for (a) 18 hours and (b) 45 hours, before (curve 1) and after annealing (curve 2)

Demagnetisation curves in the X,Y (radial) direction for the present H D magnets aligned and subsequently pressed in an isostatic press shown very poor magnetic properties. All the magnets prepared via the HD process showed uniaxial anisotropy in the direction of alignment Z. The absence of radial alignment can be attributed to the lower hydrogenation pressure of 10 bar used in the present work giving a lower hydrogen content than that reported in Ref.[7] and lattice parameters measurements using X-ray diffraction revealed that the alloy decrepitated at 10 bar had a formula unit of $Pr_2Fe_{14}BH$ assuming a linear variation of volume with H content. X-ray diffraction also confirmed that the direction of magnetization of the present HD sintered magnets lies in the c-axis.

4. CONCLUSIONS

The intrinsic coercivity of Pr-Fe-B and Pr-Fe-B-Cu sintered magnets can be increased substantially by annealing. Magnets based on $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ when annealed exhibit a iHc peak at lower milling times than $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$, $Pr_{16}Fe_{76}B_8$ and $Pr_{16.9}Fe_{79.1}B_4$ magnets. $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD sintered magnets prepared from powder of as-cast ingot and homogenized alloy obtained after low milling times exhibit different magnetic properties but their magnetic properties converge when prepared from powder obtained after milling for nine hours. This behaviour can be attributed to the rehomogenization of the cast structure after milling for the extended period and then sintering. Isostatically pressed magnets of Pr-Fe-B-Cu alloys produced by the HD process at 10 bar of H_2 are shown to exhibit uniaxial anisotropy.

5. ACKNOWLEDGMENT

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