The Effect of Annealing on the Magnetic Properties and Microstructures of Pr-Fe-B-Cu HD Sintered Magnets (1)

Luis Filipe C. P. de Lima (2)
Hidetoshi Takiishi (2)
Rubens N. de Faria Jr. (2)

X. J. Yin (3)
J. S. Abell (3)
I. R. Harris (3)

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 1273 K, resulted in an increase in iHc from 858 kAm^{-1} (~11kOe) to around 1570 kAm^{-1} (~20 kOe). The microstructures of both as-sintered and annealed magnets have been investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM) in an attempt to reveal the reason for this increase. Backscattered electron image on SEM and energy dispersive X-ray analysis (EDX) indicated the presence of Pr_2Fe_{17} (Fe : Pr (at.%) ≈ 8.2) in both magnets. The presence of this phase has been confirmed by thermomagnetic analysis and TEM investigations. The amount of this phase diminished after the heat treatment. A $Pr_{34}Fe_{62}Cu_4$ phase has also been observed by TEM. The increase in the coercivity on annealing has been attributed to the improved magnetic isolation of the $Pr_2Fe_{14}B$ grains, to the diminution in the amount of Pr_2Fe_{17} phase and to the formation of individual and isolated grains of this phase.

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(2) Instituto de Pesquisas Energéticas e Nucleares IPEN - CNEN, CEP 05422-970 , São Paulo-SP

(3)School of Metallurgy and Materials, University of Birmingham, Edgbaston, B15 2TT, UK

INTRODUCTION

For many years, hydrogen decrepitation has been employed in the processing and characterization of Nd-Fe-B sintered permanent 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[3,4]. Very recently, the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy has been found to exhibits iHc values of 795-955 kAm^{-1} (10-12 KOe) in the cast ingots after annealing[5]. In the present work, sintered magnets of composition $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ 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 microstructures of HD sintered permanent magnets have been investigated using optical metallography, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). This study has been carried out on both as-sintered and high temperature annealed magnets. Thermomagnetic analysis (TMA) and differential thermal analysis (DTA) have also been employed in the present investigations.

EXPERIMENTAL

The alloy investigated in this work has been provided by Rare Earth Products Ltd. The alloy was prepared in a rectangular (20x10x3 cm) water cooled copper mould, and the chemical analysis of the alloy is given in table 1. 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 1333 K for 1 hour and furnace cooled (cooling rate of approximately 3.5 $Kmin^{-1}$). The as-sintered magnets then received a post sintering heat treatment[6] under vacuum at 1273 K for 24 hours (also furnace cooled) and their magnetic properties were determined in a permeameter.

The microstructural observations and microanalysis were carried out using an optical microscope, a JEOL 840A scanning electron microscope (+EDX) and a JEOL 4000FX transmission electron microscope (+EDX). Samples for optical microscopy were etched with nital in order to reveal the grain boundaries and 2/17 phase. In order to prepare the TEM specimens, thin slices were cut from the magnets and the discs for TEM were then mechanically ground, dimpled to a thickness of approximately 80 μm and finally thinned by argon ion beam milling at 5-6 KeV. Thermomagnetic analysis was carried out in a Sucksmith balance using liquid nitrogen as the coolant for the low temperature studies. Differential thermal analysis (DTA) was also employed in the present work using a Linseis LDT2.

RESULTS AND DISCUSSION

The effects of milling time and annealing at 1273 K for 24 hours are shown in Fig.1. 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.1), the magnet exhibits appreciable coercivity. The magnetic properties of the magnets prepared with powder milled for 9 hours are given in Table 2 and the demagnetization curves are shown in fig. 2.

The optical metallography of the as-sintered $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnet is shown in Fig.3a, and the microstructure of this magnet after annealing at 1273 K for 24 hours and then slow cooling at a rate of 3.5 K min^{-1} is shown in fig 3b. Both samples were etched since the second phase (Pr_2Fe_{17}) was not visible in the polished condition. In the as-sintered state, this magnet consists of the $Pr_2Fe_{14}B$ matrix phase, the Pr-rich material in the grain boundaries and a dark grey phase (Pr_2Fe_{17}) within the matrix phase (the chemical analysis is discussed later). After the annealing treatment, the amount of the dark grey phase diminished and the grain boundaries became much more defined. This could indicate that the coverage of the matrix phase with a non ferro-magnetic Pr-rich material is improved after the post sintering heat treatment and this would enhance the intrinsic coercivity since better magnetic isolation of the $Pr_2Fe_{14}B$ grains would be achieved.

In the annealed condition, as indicated by fig.3b, the Pr_2Fe_{17} phase appears more as individual grains and in isolated regions. A comparison between these two microstructures also demonstrates that, rather surprisingly, there has been no significant grain growth during the post sintering heat treatment. It has been suggested[7] that the Pr_2Fe_{17} phase retards the grain growth of the $Pr_2Fe_{14}B$ matrix phase. No clear evidence of free iron and of a grain boundary eutectic observed in cast material[8] has been found in these sintered magnets .

Figure 4a and b shows a back scattered electron image of the as-sintered and annealed magnets. The presence of the dark phase (Pr_2Fe_{17}) is also observed in both samples, which is consistent with the optical microscope results. It can be seen clearly in fig. 4a that the dark phase is distributed within the matrix phase and since the backscattered electron image reveals the difference between the average atomic numbers of the phases, the differences in contrast show that the phases have different compositions. Fig. 4b indicates that, after annealing, the dark phase is more concentrated in the form of isolated grains and this is consistent with the optical microscope examinations. EDX microanalysis indicates that the dark phase is richer in iron than the matrix phase and the matrix phase showed Fe:Pr at. ratio of about 7 and the dark phase Fe : Pr at. ratio of approximately 8.2 indicating a 2 : 17 type phase. This is consistent with previous studies[7] , which have shown that, in sintered magnets of the $Pr_{17}Fe_{83-x}B_x$-type, the magnetically soft Pr_2Fe_{17} phase always occurs when $x < 5$. An equivalent Nd_2Fe_{17} magnetically soft phase has also been found in Nd-based sintered magnets with similar compositions[7,9,10]. It has been shown[9] that the amount of this phase (Nd_2Fe_{17}) was reduced with a high temperature heat treatment. According to this work[9], some of the 2 : 17-type phase was removed during the high temperature heat treatment and this is consistent with the present observations for the Pr-based magnets. No other phases could be detected by the SEM.

Thermomagnetic curves for the as-sintered and annealed magnets are presented in figs.5a and 5b. The small magnetisation variation (between 350 to 500 K) can be ascribed to the competing effects of increasing temperature on the degree of saturation of the sample (due to decreasing anisotropy of the sample which is misaligned slightly with respect to the field) and the value of the saturation magnetisation. The TMA curves of both magnets showed that, in addition to the matrix phase (Tc=555 K), there was a lower Curie point ferromagnetic phase in both magnets with a Tc around 304 and 310 K, and this can be attributed to the presence of a 2 : 17 type phase in these magnets, consistent with the SEM observations. This phase (Pr_2Fe_{17}) has a reported Curie point as low as 283 K[11] and 288 K[7], and as high as 301 K[12]. It has also been reported[12] that when free Fe is present the Curie point of this phase varies from 315 to 323 K (free iron has not been detected in the present magnets). The initial Curie point minimum in fig. 5b is significantly less pronounced than that in fig. 5a, indicating a possible reduction in the amount of the 2 : 17 phase after the annealing treatment.

The Curie temperature of the matrix phase determined by DTA was around 563 K (see fig. 6a and b). This value is slightly higher than that determined by TMA. This phase also has various reported Curie temperatures such as 576 K[13], 563 K[14] and 557 K[15]. In fig. 6a and 6b, at around 736 K, there is the possibility of a small peak, which could be related to the melting temperature of the Pr-rich eutectic grain boundary phase (723 K[8] and 734 K[15]). This eutectic phase has been found in the grain boundaries of the as-cast alloy after annealing[8] and the DTA studies on this material showed an appreciable peak at 723 K, due to the melting of this phase. In the present studies on sintered magnets there is no clear evidence for the presence of the eutectic phase either from the DTA or from optical metallography and SEM studies. The finer grain size of the sintered magnet and hence more evenly distributed grain boundary phase would make it more difficult to resolve the eutectic mixture (if present). It should also be noted that the oxygen content of the sintered magnet will be significantly greater than that of the cast material and this should lead to a modification of the grain boundary phases. In the "as-sintered" condition the DTA curve shows a well defined peak around 940 K and this peak can be ascribed to the $Pr_2Fe_{14}B$-Pr eutectic isotherm at 949 K[14]. However, this peak is not observed in the annealed condition, thus indicating a change in the nature of the grain boundary phases after this treatment.

Transmission electron microscopy studies confirmed that the annealed $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnets contain a phase with a Fe : Pr at. ratio of ~ 8.6 (2 : 17) and this is consistent with the SEM analysis (Fig. 7 shows the analysed region). TEM observations also showed the presence of a $Pr_{34}Fe_{62}Cu_4$ phase in the annealed sample and Fig. 8 shows the TEM analysed region of this phase. A phase with a very similar composition has also been found in the cast alloy after annealing[8,16] and has been reported[17] recently in hot pressed magnets as a $Pr_6Fe_{13}Cu$-type phase. A similar Cu containing phase has also been found in $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ sintered HD magnets[9,18] and a similar phase has been observed first in Nd-Fe-Si and Nd-Fe-Al alloys[19,20].

It has been shown by DTA studies[17] on an annealed $Pr_{32.5}Fe_{62}Cu_{5.5}$ alloy that the Pr_2Fe_{17} phase and the liquid phase are stable above 918 K and a $Pr_6Fe_{13}Cu$ phase is formed below 918 K by a peritectic reaction : Pr_2Fe_{17} + Liq. —> $Pr_6Fe_{13}Cu$. According to this work the $Pr_6Fe_{13}Cu$ phase crystallizes during holding at 753 K. It has been shown[21] that the iHc of annealed and fast-cooled (100Kmin^{-1}) $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnets is lower than that of the slow-cooled (3.5 Kmin^{-1}) magnets, indicating that slow cooling is also important for increasing iHc.

Further annealing of the present magnets at 773 K for 3 hours did not result in change in the intrinsic coercivity, indicating that full iHc has been achieved with slow cooling after annealing at 1273 K. Annealing at this temperature resulted in an increase in iHc from 858 to 1392 KAm^{-1} (Δ=534) whereas slow cooling was responsible for a further increase from 1392 to 1570 KAm^{-1} (Δ=178). The present work indicates that the amount of Pr_2Fe_{17} phase is reduced with the heat treatment at 1273 K (as in the case of the Nd_2Fe_{17} phase in Nd-Fe-B-Cu HD magnets[9]) and during slow cooling some of this phase is also transformed into the $Pr_{32.5}Fe_{62}Cu_{5.5}$-type phase (as in the case of the Pr-Fe-B-Cu hot pressed magnets[17]). Bearing in mind that, in Cu-free Pr-Fe-B HD magnets[21], there was also a similar increase in iHc on annealing at 1273 K, it is most likely that in both cases, iHc increases as a result of a combination of factors, (a) an improved magnetic isolation of the $Pr_2Fe_{14}B$ grains, (b) a reduction in the amount of the Pr_2Fe_{17} phase and (c) formation and isolation of individual Pr_2Fe_{17} grains. The smoothing of the grain boundaries could also be a contributory factor (as reported in the case of cast $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnets[16]). The presence of the $Pr_6Fe_{13}Cu$-type phase is indicative of a further reduction in the amount of the Pr_2Fe_{17} phase and this could be why the former is associated with an improvement in coercivity. The similarity in the coercivity behaviour of the Cu-free Pr-Fe-B HD magnets[21] to the present ones on annealing at 1273 K and slow cooling , indicates that the presence of the $Pr_6Fe_{13}Cu$-type phase may only result in a small additional improvement in the coercivity due to some improved magnetic isolation of the matrix phase.

CONCLUSIONS

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. The amount of the Pr_2Fe_{17} phase 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 this phase is closely associated with the matrix phase whereas after annealing it occurs as individual isolated grains. A $Pr_{34}Fe_{62}Cu_4$ phase has been identified in a magnet annealed at 1273 K for 24 hours and then slow cooling but the similar coercivity behaviour of a Cu-free, $Pr_{17}Fe_{79}B_4$ magnet on annealing at 1273 K indicates that the presence of such a phase may only result in a small additional improvement in the coercivity.

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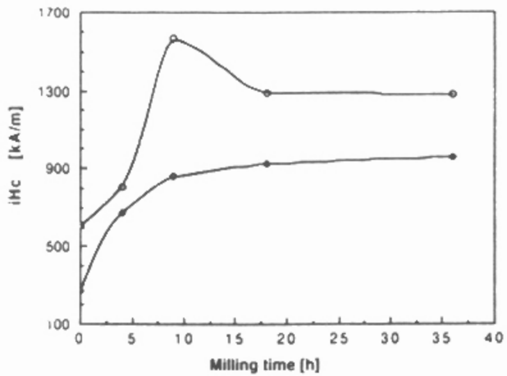


Fig.1 Variation of iHc with milling time for slowly cooled magnets of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy. (◊ : As-sintered, o: annealed 1273 K, 24h)

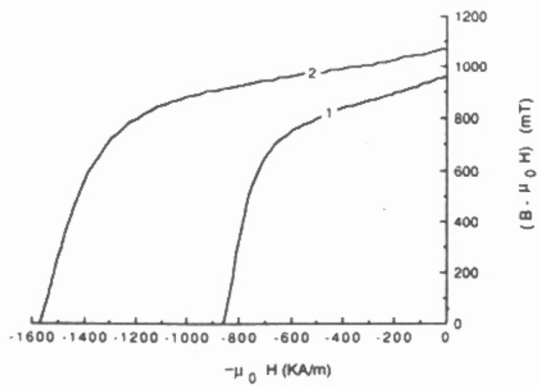
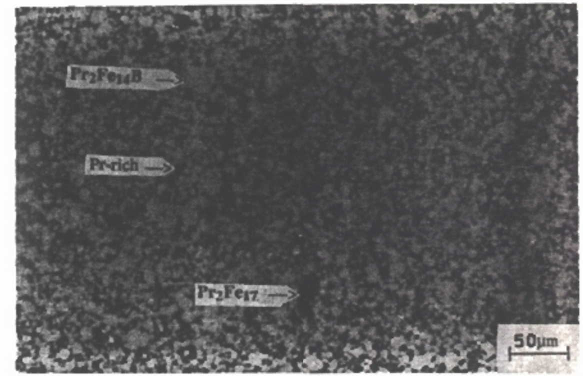


Fig.2 The demagnetization curves for slow cooled $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnets, before (1) and after annealing (2). (milling time : 9 hours)

(a)



(b)

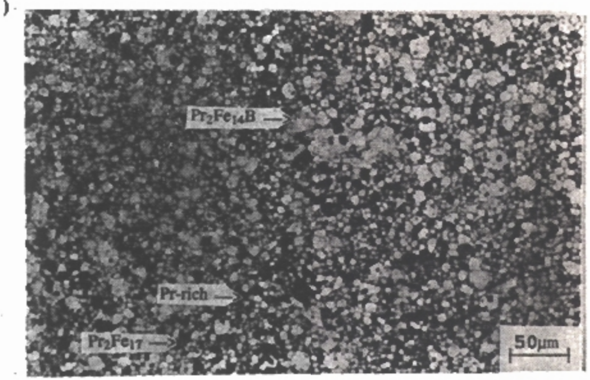


Fig.3 Optical micrograph showing a general view of the microstructure of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnet in the as-sintered (a) and annealed (b) condition (Black regions : grains pulled out on polishing or on etching with nital).

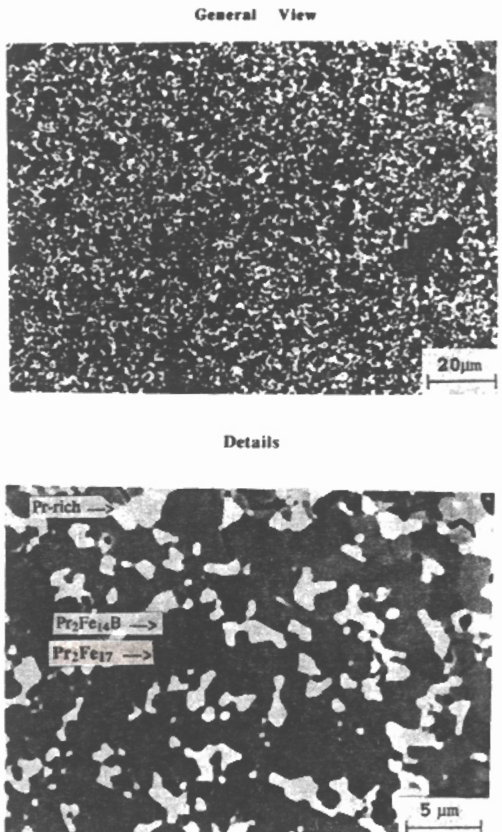


Fig. 4a Back scattered electron image of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnet in the as-sintered condition.

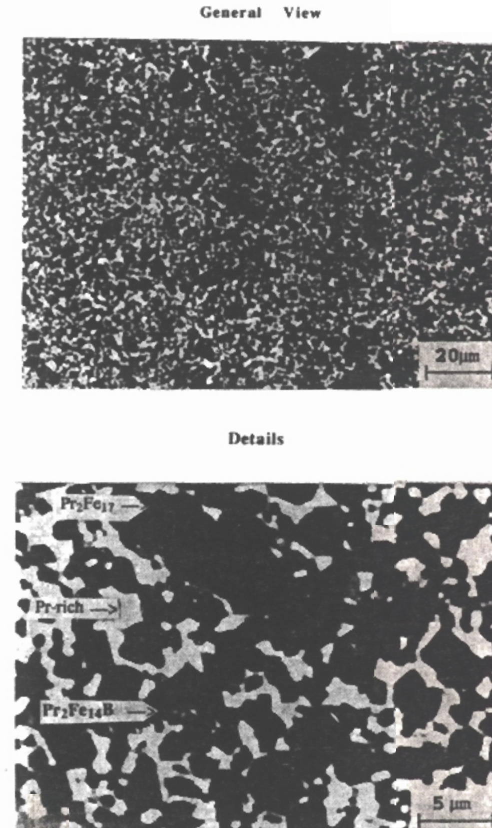
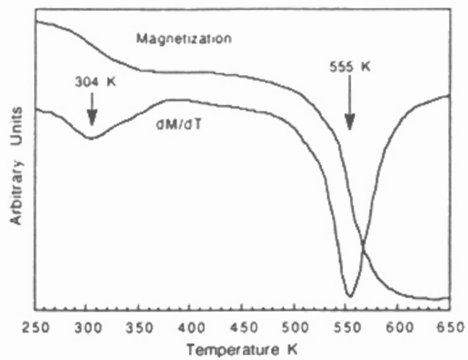


Fig. 4b Back scattered electron image of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnet in the annealed condition. In the as-sintered condition the Pr_2Fe_{17} phase is embedded in the matrix phase ($Pr_2Fe_{14}B$), whereas after annealing at 1273 K for 24 hours and then slow cooling it occurs as individual isolated grains.



(b)

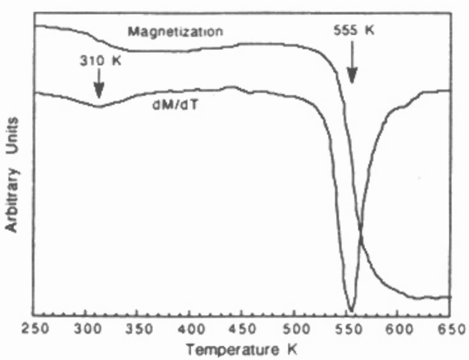
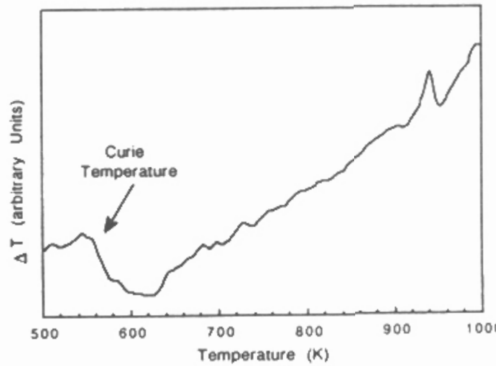


Fig.5 Magnetisation (non-saturated) versus temperature for the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnet in the as-sintered (a) and annealed condition (b) (error ± 5K).



(b)

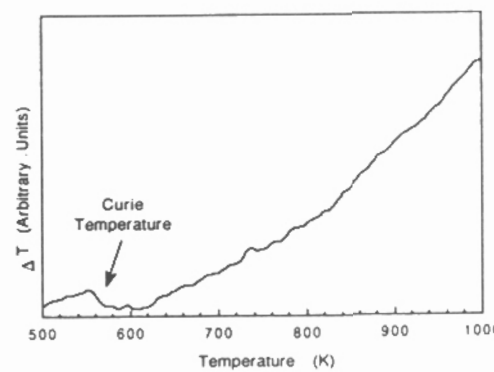


Fig.6 DTA heating curve for as-sintered (a) and annealed (b)$Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet prepared using the HD process (error ± 7 K).

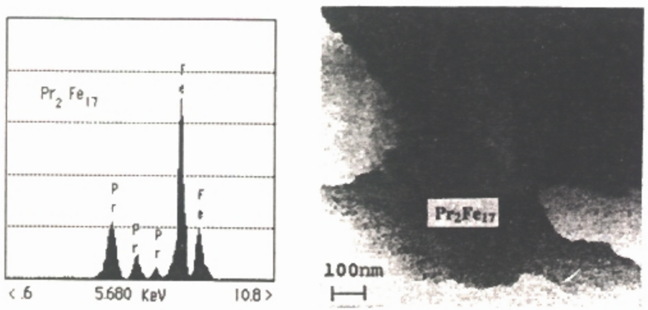


Fig. 7 Transmission electron micrograph and X-ray spectrum of a Pr_2Fe_{17} phase (annealed magnet).

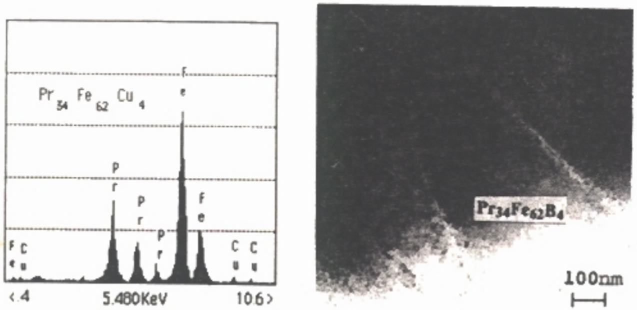


Fig.8 Transmission electron micrograph and X-ray spectrum of a $Pr_{34}Fe_{62}Cu_4$ phase (annealed magnet).

Table 1. Chemical analysis of the as-cast alloy.

Atomic %	Wt %			
	Pr	Fe	B	Cu
$Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$	40.0	Bal.	0.60	1.60

Table 2 Magnetic properties of $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD sintered magnets

Magnet condition	Br (mT)	iHc (KAm^{-1})	$(BH)_{max}$ (KJm^{-3})
As-sintered	960±10	858±20	147±6
Annealed*	1070±8	1570±12	198±10

*(1273 K for 24 h)