X-ray Determination of Crystal Alignment in Pr-Fe-B Sintered Magnets Produced from Hydride Powder and from Partially and Totally Desorbed Hydride Powder

N. B. LIMA , M. M. SERNA, H. O. SANTOS, R. N. FARIA
Instituto de Pesquisas Energéticas e Nucleares IPEN - CNEN, CEP 05422-970 , São Paulo-SP.

A. J. WILLIAMS and I. R. HARRIS
School of Metallurgy and Materials, University of Birmingham, Edgbaston, B15 2TT, UK

Abstract

The influence of partial and complete desorption of the hydrided powder prior to magnetic processing on the final magnetic properties of HD sintered magnets of a $Pr_{16}Fe_{76}B_8$ alloy has been investigated. The alignment of these sintered magnets have been investigated by X-ray diffraction. A study to correlate the magnetic behaviour with the degree of crystal alignment has been carried out. The standard deviation (σ) of the Gaussian distribution has been used as an indicator for the crystal alignment of the $Pr_{16}Fe_{76}B_8$ sintered magnets. Sintered magnets produced from the the totally desorbed powder (Br~12.2 kG, $(BH)_{max}$~36.0 MGOe and iHc~10.6 kOe) exhibit a narrower Gaussian distribution (σ=14.8°) compared to that of magnets prepared from the hydrided powder (σ=41.2°, Br~10.9 kG, $(BH)_{max}$~29.1 MGOe and iHc~17.5 kOe), showing the better crystal alignment in the former. Attempts have been made to correlate the remanences of various Pr-Fe-B sintered magnets with their corresponding intrinsic coercivities.

Introduction

The initial microstructure of Nd-Fe-B as-cast ingots has been found to play a role in the final magnetic properties of sintered magnets[1,2,3]. Recent work[4] has shown the influence of the alloy state on the final magnetic properties of $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD sintered permanent magnets. In these investigations[1-4] the microstructures were modified by changing the cooling rate of the ingot[1,2], by a vertical floating-zone technique[3] and by an ingot homogenization heat treatment[4]. In the present work the possible influence of the partial and complete desorption of the hydrided powder on the final magnetic properties of HD sintered magnets of a $Pr_{16}Fe_{76}B_8$ alloy has been investigated. X-ray diffraction has been used to correlate the magnetic behaviour and the degree of crystal alignment of these magnets.

The alignment of magnets can be determined by X-ray diffraction and fitting the standard deviation of a Gaussian distribution for the relative intensity versus the angle between the normals of (*hkl*) and the tetragonal c axis[5,6]. Although several methods have already been proposed to evaluate the crystal alignment of magnets[7,8,9,10,11], in the present work, the crystal alignment of the $Pr_{16}Fe_{76}B_8$ magnets has been investigated using the method described in Refs. 5 and 6.

Recent studies in RE-Fe-B sintered magnets[12,13] , have shown that an improved grain alignment leads to a reduction of coercivity due to an increase of internal demagnetizing fields. It has also been reported[14] that the commonly observed decrease of coercivity with improved grain alignment is not an inevitable correlation in RE-Fe-B magnets and that in materials with high coercivity (compared to the theoretical nucleation field), an improved grain alignment should also lead to an increase in the coercive field. In the present work, attempts have been made to correlate remanence and intrinsic coercivity of various Pr-Fe-B permanent magnets. A comparison of various permanent magnets, processed by standard powder metallurgy route, HD process, hot pressing and hot rolling, has also been provided.

Experimental

The alloy investigated in this work was provided by Rare Earth Products Ltd., Widnes, UK. The alloy, of composition $Pr_{16}Fe_{76}B_8$ (atomic%), was prepared in a rectangular (20x10x3 cm) water cooled copper mould. In order to produce the magnets via the HD process, small pieces of the bulk ingot (without heat treatment) were placed in a stainless steel hydrogenation vessel which was then evacuated to backing-pump pressure and hydrogen was then introduced to a pressure of 10bar. This resulted in decrepitation of the bulk material and the decrepitated material was evacuated to backing-pump pressure for 1 hour and 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 under dry nitrogen to a small cylindrical rubber tube, pulsed in a magnetic field of 4.5 T and isostatically pressed. The resulting green compacts were vacuum sintered at 1060°C for 1 hour followed by a furnace cool (~3.5°C/min) and a post sintering heat treatment (first used in cast magnets) under vacuum at 1000 °C for 24 hours and the magnetic properties measured in a permeameter. The annealing treatment was first employed by Shimoda et al[15] in cast and hot pressed magnets based on the composition $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$.

The desorption behaviour of hydrogen from the $Pr_{16}Fe_{76}B_8$ alloy (small lumps of the cast ingot) was investigated using a mass spectrometer described elsewhere[16,17], which indicated the appropriate temperatures for partial and total desorption of the powder. Partially desorbed powder was prepared from the decrepitated hydride by a heat treatment in vacuum at 300°C for 5 hours. Total desorption of the material was also carried out in vacuum but at 600°C for 5 hours. The partially and totally desorbed material was then processed in the same manner as the decrepitated hydride material.

A Rigaku diffractrometer was used in the measurements of the diffraction intensities (CoKα). The $Pr_{16}Fe_{76}B_8$ cast alloy (powder) was used as an isotropic reference pattern. The relative intensity was determined by measuring the ratio of peak heights of the anisotropic Pr-Fe-B sintered magnets to those of the corresponding isotropic reference. Similarly to Refs. 5 and 6, this relative intensity was then plotted against the angle θ, the angle between the normal of (*hkl*) and the tetragonal c axis. This data was then fitted to a Gaussian distribution to obtain a standard deviation σ , which then acts as an indicator for the crystal alignment.

Results and Discussion

The hydrogen desorption curve for the $Pr_{16}Fe_{76}B_8$ alloy is shown in fig. 1 and consists of two desorption events, one centred on approximately 145 °C and the other centred around 580°C. There is a slight shoulder on the right-hand side of the lower temperature

desorption peak which is similar to that of desorption studies[16] on a $Nd_{16}Fe_{76}B_8$ alloy. From these studies the low temperature peak observed in the present work can be ascribed to the full desorption of hydrogen from the $Pr_2Fe_{14}B$ phase and the shoulder on the right of this peak to the partial desorption of hydrogen from the rare earth rich grain boundary phase. The higher temperature peak can be ascribed to the complete desorption of hydrogen from the Pr-rich phase at around 580°C .

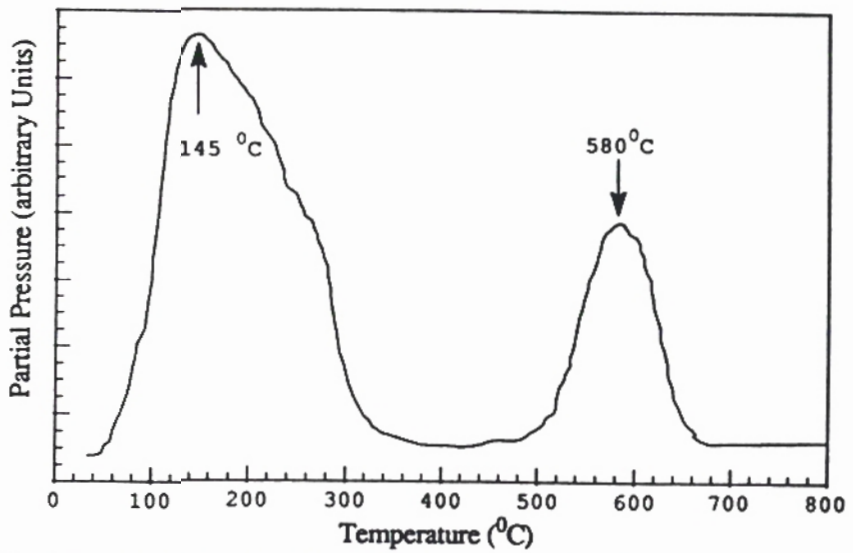


Fig. 1 Mass spectrometer desorption trace of $Pr_{16}Fe_{76}B_8$ alloy, hydrided in-situ and heated at 4°C/min.

The demagnetization curves for magnets produced from hydride powder and from partially and totally desorbed hydride powder are shown in fig.2. The effect of complete desorption of the HD powder prior to magnetic processing was to increase the remanence and decrease the intrinsic coercivity (curve 3) of the sintered magnets compared with the corresponding properties of the standard HD magnet subjected to the same milling and heat treatments (curve 1). In this case an improved energy product of 36 MGOe was achieved. The effect of partial desorption of the HD alloy prior to magnetic processing was also to increase the remanence and to decrease the intrinsic coercivity (curve 2) but both to a lesser extent than in the previous case. A very square loop is obtained for this magnet and the best overall magnetic properties are achieved in this case. The magnetic properties of these annealed magnets are summarized in Table I.

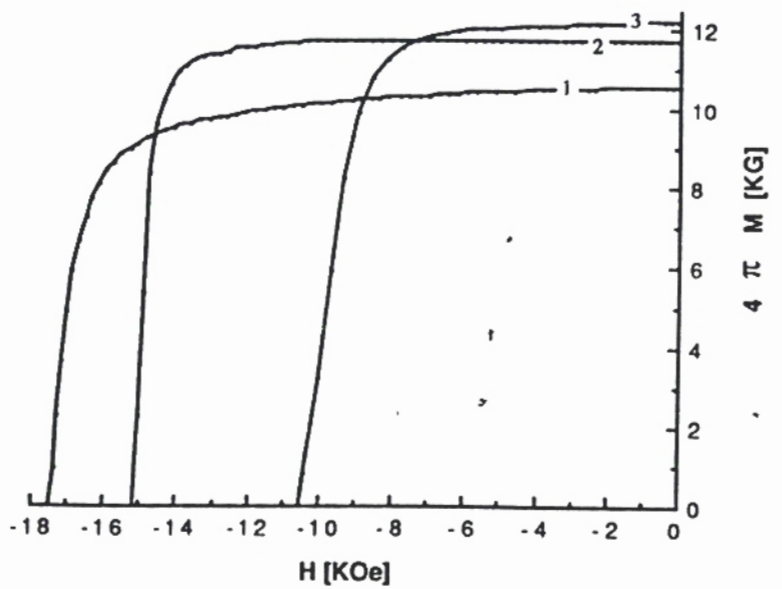


Fig. 2 Demagnetization curves for annealed $Pr_{16}Fe_{76}B_8$ sintered magnets prepared using (1) the HD powder, (2) partially desorbed HD powder and (3) totally desorbed HD powder, all milled for 18 hours and annealed at 1000 °C for 24 hours (slowly cooled) after sintering .

Table I. Comparison of various annealed $Pr_{16}Fe_{76}B_8$ sintered permanent magnets produced in the present work (PD=partially desorbed and TD=totally desorbed).

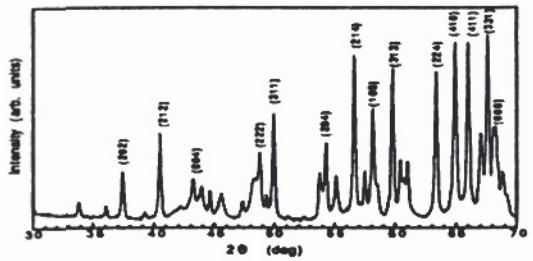
Alloy Condition	Br KG	iHc KOe	bHc KOe	(BH) max MGO	S.F
HD	10.9	17.5	10.5	29.1	0.81
PD	11.7	15.2	11.6	35.2	0.93
TD	12.2	10.6	8.9	36.0	0.80

(Average error: Br : ± 0.1, iHc : ± 0.5, (BH)max : ± 0.9)

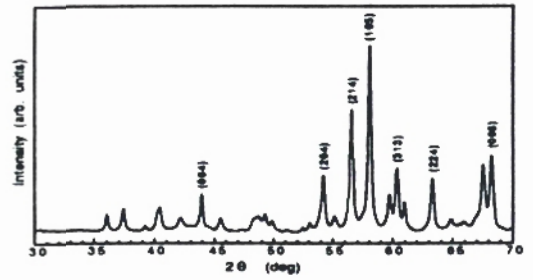
The X-ray diffraction pattern of an unaligned powder of the $Pr_{16}Fe_{76}B_8$ alloy is shown in fig. 3a. This spectrum agrees well with that presented by Rotenberg et al[18] for an ingot of $Pr_2Fe_{14}B$. Figure 3b shows the X-ray diffraction pattern of a sintered $Pr_{16}Fe_{76}B_8$ magnet prepared from HD powder. The intensity of the (105) reflection is enhanced compared to the (214) reflection, showing, as expected, crystal alignment in this magnet. Figure 3c shows

the X-ray diffraction pattern of a sintered $Pr_{16}Fe_{76}B_8$ magnet produced from partially desorbed HD material. In this case the well aligned sample shows three strong peaks: (004), (105) and (006), where the (004) and (006) planes are perpendicular to the easy direction [001] in the tetragonal crystal structure of the matrix phase, the (105) is tilted by about 15° from the (00n) plane and the (006) reflection is the strongest one[8]. Figure 3d shows the X-ray diffraction pattern of a sintered $Pr_{16}Fe_{76}B_8$ magnet produced from totally desorbed HD material. In this case there is no significant difference from the previous X-ray diffraction pattern. A similar X-ray diffraction pattern has also been observed in a $Pr_{17}Fe_{79}B_4$ HD sintered magnet[19] and hot pressed magnets[20] based on the composition $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$.

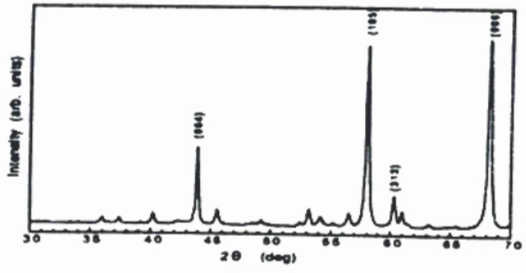
The correlation between the relative intensity and the angle (θ), the fitted Gaussian distribution and the standard deviations for the HD and PD magnets is shown in fig. 4a and b respectively. The sintered $Pr_{16}Fe_{76}B_8$ magnet produced from partially desorbed HD material has a narrow Gaussian distribution with a standard deviation (σ) of 14.8° whereas the magnet produced from HD material has a broad Gaussian distribution with a standard deviation of 41.2°. This demonstrates that a better crystal alignment is obtained in the former. As expected, no significant difference has been found for standard deviation of the magnet produced from partially and totally desorbed HD material.



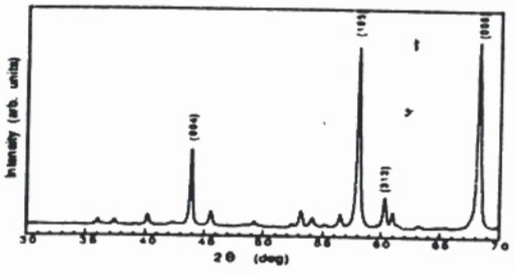
(a)



(b)



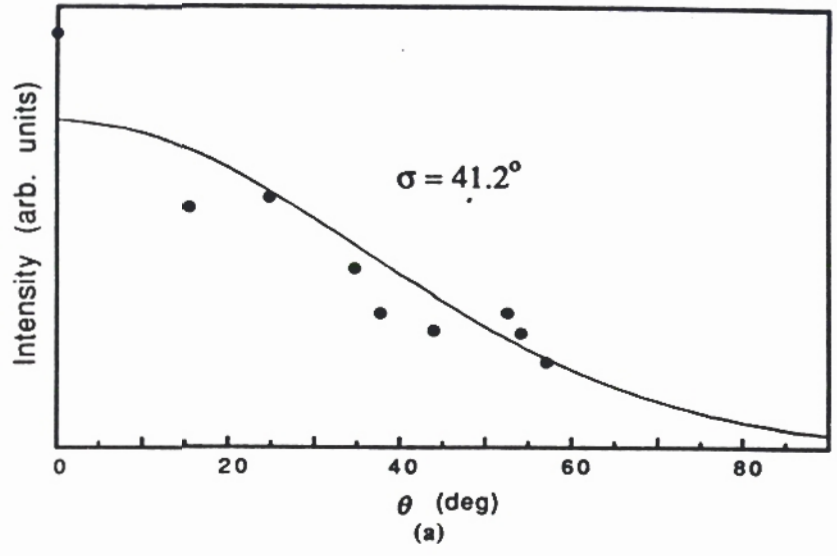
(c)



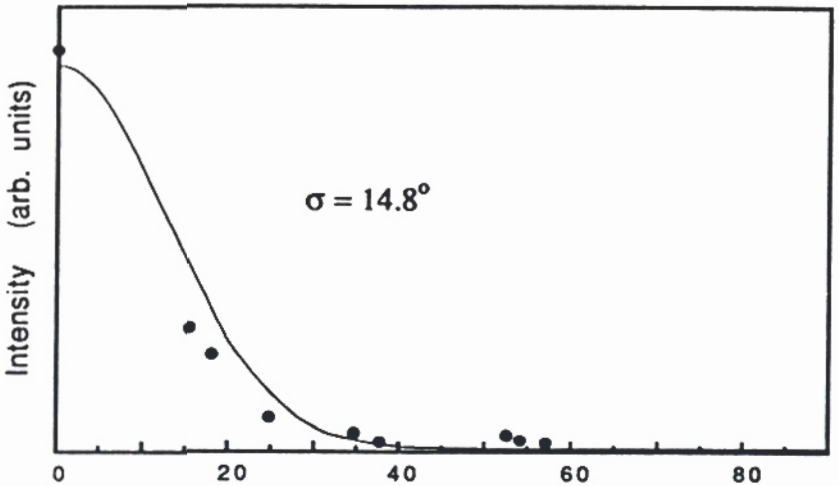
(d)

Fig.3 X-ray diffraction patterns of $Pr_{16}Fe_{76}B_8$ alloy and magnets. a) As-cast alloy, b) HD magnet, c) PD magnet and d) TD magnet.

It is known that hydrogen reduces the uniaxial magnetocrystalline anisotropy factor of the phase $Pr_2Fe_{14}B$ such that it is possible to change from easy axis to easy plane between $Pr_2Fe_{14}B$ and $Pr_2Fe_{14}BH_5$ (60 bar of H_2)[21]. Under the hydrogenation conditions used in the present work (10 bar of H_2), an intermediate hydrogen content would be attained and a reduced uniaxial anisotropy factor would be expected. This would reduce the torque producing alignment in the powder compacts and hence a reduction in the overall degree of crystal alignment would be expected. This reduction in the degree of alignment is confirmed by the present results of X-ray diffraction. This interpretation is also consistent with studies[22] on some $RE_2Fe_{14}BH_x$ compounds (RE = Y, Ho and Nd) which have reported a steady decrease in the uniaxial anisotropy constant with increasing hydrogen content.



(a)



(b)

Fig.4 Relative intensity vs θ , the angle between the tetragonal c axis and the normal of the (hkl) plane for the a) HD and b) PD magnets.

It has been shown, using Mössbauer spectroscopy analysis in $RE_2Fe_{14}BH_x$ compounds, that spin reorientation is induced by hydrogen[23]. The rotation begins for hydrogen concentrations between 2 and 3 H per formula unit for the Pr and Gd compounds with $\Phi_{max} = 55 \pm 10°$. Under the hydrogenation conditions used in the present work, an intermediate hydrogen content would be attained and a partial rotation could be expected. Consequently some additional crystal misalignment of the c-axis in the sintered magnets would occur with a reduced remanence.

Table II. Comparison of various PrFeB-type permanent magnets.

ALLOY TYPE		PC	Br KG	iHc KOe	BH MGO	Ref.
$Pr_{15-x}Dy_xFe_{62.5}Co_{16}Al_1B_{5.5}$	x=0	PM	12.7	9.6	38.0	24
	x=1		12.3	11.5	34.6	
	x=2		11.5	14.3	32.1	
	x=3		11.2	17.1	30.5	
	x=4		10.4	22.0	26.2	
$Pr_{15-x}Tb_xFe_{62.5}Co_{16}Al_1B_{5.5}$	x=0	PM	12.7	9.6	38.0	24
	x=1		11.8	13.8	32.5	
	x=2		11.3	15.2	31.1	
$Pr_{15}Fe_{79}B_6$		PM	12.9	12.4	39.4	24
$Pr_{16}Fe_{76}B_8$		HD	10.9	17.5	29.1	This Work
		PD	11.7	15.2	35.2	
		TD	12.2	10.6	36.0	
$Pr_{16.9}Fe_{79.1}B_4$		HD	10.6	20.3	25.3	19
$Pr_{17}Fe_{76.5}B_5Cu_{1.5}$		HP	12.6	10.0	36.2	20
$Pr_{17}Fe_{76.5}B_5Cu_{1.5}$		HR	11.0	16.2	28.4	25
$Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$		HD	10.7	19.8	24.9	19

(PC : processing conditions, HP: hot-pressed, HR: hot-rolled, PM: powder metallurgy)
(Average error: Br : ± 0.1, iHc : ± 0.5, (BH)max : ± 0.9)

A comparison of magnetic properties of various permanent magnets is given in Table II. The magnets were produced using various processing routes and conditions. It can be noted that the highest energy product is obtained with a magnet of an alloy of $Pr_{15}Fe_{79}B_6$ whereas the highest intrinsic coercivity is achieved with a composition of $Pr_{11}Dy_4Fe_{62.5}Co_{16}Al_1B_{5.5}$. Plotting remanence versus coercivity for all the magnets given in table II, gives, an empirical, straight line relationship, as shown in fig. 5, i.e., the remanence decreases linearly with increasing intrinsic coercivity. Table III shows the magnetic properties of the present magnets before the optimal heat treatment. In this case full magnetic properties have not been reached and there is a poor fit with the relationship shown in fig. 5.

TableIII. Magnetic properties of the present $Pr_{16}Fe_{76}B_8$ magnets before annealing at 1000 °C for 24 hours.(Average error: Br : ± 0.1, iHc : ± 0.5, (BH)max : ± 0.9)

Alloy Condition	Br KG	iHc KOe	bHc KOe	(BH) MGOe	S.F
HD	10.9	14.9	10.2	29.4	0.77
PD	11.3	14.5	10.0	31.0	0.66
TD	12.0	9.9	8.4	31.8	0.73

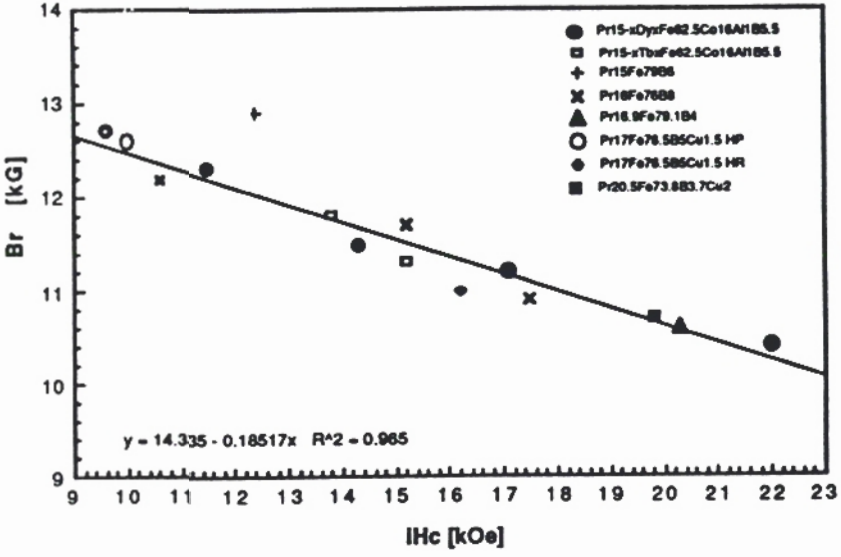


Fig.5 Empirical correlation between remanence and intrinsic coercivity of various permanent magnets.

Conclusions

$Pr_{16}Fe_{76}B_8$ sintered magnets prepared from milled HD powder and from milled partially and totally desorbed HD material exhibit different magnetic properties. The intrinsic coercivity is higher in the sintered magnets prepared using milled HD material whereas the remanence and energy product are higher in the magnets produced from milled partially and totally desorbed HD material. The degree of crystal alignment is higher in the sintered magnets produced from partially and totally desorbed HD material when compared to that of magnets produced from HD material. The alignment of the $Pr_{16}Fe_{76}B_8$ sintered magnets was determined by fitting the relative intensity of certain (*hkl*) planes and the angles between their normal and the tetragonal c axis for a Gaussian distribution. The standard deviation of the Gaussian distribution, employed as an indicator for the alignment, was lower (σ = 14.8°) in the magnets produced from milled partially and totally desorbed HD material. The difference in the degree of alignment of the milled powders was attributed partially to the reduced anisotropy of the $Pr_2Fe_{14}B$ phase in the HD powder. It has also been shown that there is a

good linear relationship between Br and iHc holds only for a wide range of Pr-Fe-B-type magnets.

Acknowledgements

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Spin Wave Gap in $Pr_2Fe_{14}B$

I KLEINSCHROTH and H KRONMÜLLER. Institut für Physik, Max-Planck-Institut für Metallforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

Abstract

In order to study the influence of the magnetocrystalline anisotropy on the spontaneous polarization, of an highly aligned sintered magnet of nominal composition $Pr_{15}Fe_{77}B_8$ polarization curves have been measured in fields up to 10 T in the temperature range between 10 and 580 K. In the reversible region of the approach to ferromagnetic saturation the spontaneous polarization could be determined by eliminating field - dependent contributions due to rotations against anisotropy (at lower temperature) and forced polarization dominant at higher temperatures. It has been found that the temperature dependence of the polarization can be described by a modified Bloch-law in terms of $T^{\frac{1}{2}}exp(\frac{-\Delta}{k_BT})$. The obtained gap energy $\Delta \sim 3.4 - 5.3$ meV is in good agreement with theoretical calculations and neutron diffraction measurements.

Introduction

The outstanding features of the $RE_2Fe_{14}B$ - compounds with RE = Nd, Pr are their large spontaneous polarization due to ferromagnetic coupling of the light rare - earth with the Fe - moments and their strong anisotropy, which, at low temperatures, is dominated by the contribution of the RE - sublattice. A main reason why $Pr_2Fe_{14}B$-compounds have been investigated in this paper is the fact that in contrast to $Nd_2Fe_{14}B$-compounds the polarization in the whole temperature range lies always in the [001] - direction. In the [100] and [110] - directions First Order Magnetization Processes (FOMPs) have beeen reported [1,2]. The occurence of FOMPs indicates that higher order terms of the anisotropy constants have to be taken into account [3]. For this reason the magnetocrystalline anisotropy should be described in terms of $\Phi_K = K_{eff}sin^2\alpha$, where α denotes the angle between spontaneous polarization $\vec{J}_s$ and $\vec{c}$-axis, and K_{eff} should be interpreted as an effective anisotropy constant including contributions of higher anisotropy constants[3]. The resulting anisotropy field due to $\mu_0 H_A = \frac{\mu_0 2K_{eff}}{J_s}$ is around 32 T at 4.2 K in $Pr_2Fe_{14}B$, whereby the temperature dependence of $\mu_0 H_A(T)$ is weak below 100 K [3]. Both the anisotropy field $\mu_0 H_A$ and the internal field $\mu_0 H$ (i.e. the external applied field minus the demagnetizing field) may be included into an effective field $\mu_0 H_{eff}$.

$$\mu_0 H_{eff} = \mu_0 H_A + \mu_0 H. \qquad (1)$$

In this paper, the anisotropy - induced spin wave gap is derived from measurements of the temperature dependence of the spontaneous polarization. The result is compared with neutron diffraction measurements and theoretical calculations.