Controlled solidification and magnetic properties of Pr-Fe-B-Cu and Nd-Fe-B alloys

R. N. Faria, J. S. Abell, and I. R. Harris
School of Metallurgy and Materials, University of Birmingham, Edgbaston, B15 2TT, United Kingdom

The as-cast microstructure of the alloys $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ and $Nd_{16}Fe_{76}B_8$ have been modified using a vertical floating-zone (VFZ) technique. By annealing the as-cast alloys and VFZ material at 1000 °C, the magnetic properties increased substantially for Pr-Fe-B-Cu alloy. VFZ growth rates up to 38 cm/h have not been sufficient to reproduce the as-cast ingot microstructure of the Pr-Fe-B-Cu alloy. Cast magnets prepared in a very small chill mold showed the best magnetic properties, with a $(BH)_{max} = 98$ kJ/m^3. Sintered magnets prepared using the hydrogen decrepitation process from the large grained Nd-Fe-B zoned alloys exhibit inferior squareness factors to those prepared from the as-cast ingot.

I. INTRODUCTION

The microstructure of Pr-Fe-B-Cu cast ingots has been found to play an important role on the magnetic properties of as-cast and hot-pressed magnets.[1,2] Previous work in the authors' laboratory has studied the influence of solidification behavior on the microstructure and hydrogen absorption of Nd-Fe-B alloys.[3] In the present work the solidification behavior of Pr-Fe-B-Cu and Nd-Fe-B alloys and the influence of the microstructure on the magnetic properties of magnets based on cast material and on sintered powder have been investigated. The effects of directional solidification (DS) processing on the magnetic properties of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy have been studied as a possible direct means of producing grain-aligned rods with enhanced hard magnetic properties. The magnetic behavior of this material was compared with that of the as-cast ingots. DS might have the advantage of being a low-cost process of preparing rare-earth/transition-metal magnets. Three steps are needed in the processing: casting, DS, and annealing. DS using the containerless vertical floating-zone (VFZ) technique is of particular interest since the alloy is almost free of contamination from the melting operation. The Pr-Fe-B-Cu alloy selected for this work contained more Pr than previously studied alloys,[1] in order to facilitate the examination of the grain-boundary regions and to assure good magnetic isolation of the individual grains.

Rods of the alloy $Nd_{16}Fe_{76}B_8$ were also directionally solidified using VFZ equipment under controlled conditions for a fixed value of the temperature gradient/growth rate ratio (G/R). Sintered permanent magnets using the hydrogen decrepitation (HD) process[4] were prepared from the VFZ material in order to try and relate the final magnetic properties with the initial state of the alloy.

II. EXPERIMENT

The as-cast ingot alloys supplied by REP (compositions are given in Table I) were prepared in rectangular ($20\times10\times3$ cm and $10\times10\times0.7$ cm) water-cooled copper molds with a cooling rate up to 600 °C/min (chill cast). In order to investigate the magnetic properties of the as-cast Pr-Fe-B-Cu alloy, the ingots were cut into cubic shape pieces using a diamond saw and then measured in a permeameter. The small pieces were then annealed at 1000 °C for 24 h and their magnetic properties were redetermined.

Rod shape material ($\phi = 5$ mm, $L = 150$ mm) was prepared from broken pieces of the Pr-Fe-B-Cu ingot by remelting them in a water-cooled copper boat[5] heated by a 350-kHz radio frequency (rf) generator. DS was carried out in the rods using a VFZ apparatus described in detail elsewhere.[6] Growth rates R from 2 to 38 cm/h and an estimated thermal gradient G of approximately 100 °C/cm were used in the VFZ experiments. Suitable cubic samples were cut from the rods and after annealing the VFZ materials at 1000 °C for 24 h, magnetic property measurements were also carried out in a permeameter.

In order to investigate the influence of the initial microstructure on the magnetic properties of Nd-Fe-B, sintered magnets were prepared from hydrogen-decrepitated (HD) material (see details in Ref. 4) via powder metallurgy from the following starting material: (1) As-cast ingot (as received from REP) and (2) VFZ material (prepared from as-cast ingot).

RESULTS AND DISCUSSION

A. Cast and VFZ Pr-Fe-B-Cu permanent magnets

The microstructures of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy, as-cast and annealed (slow cooled; 3 cm mold), are shown in Fig. 1. The obvious changes during annealing are the reduction in the amount of grain-boundary needlelike phase, the appearance of a coarse grain-boundary eutectic,

TABLE I. Chemical analysis of the as-cast alloys.

Alloy (at. %)	Pr/Nd	Fe	B	Cu (wt. %)
$Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$	40.0	Bal.	0.60	1.60
$Nd_{16}Fe_{76}B_8$	35.0	63.7	1.30	···

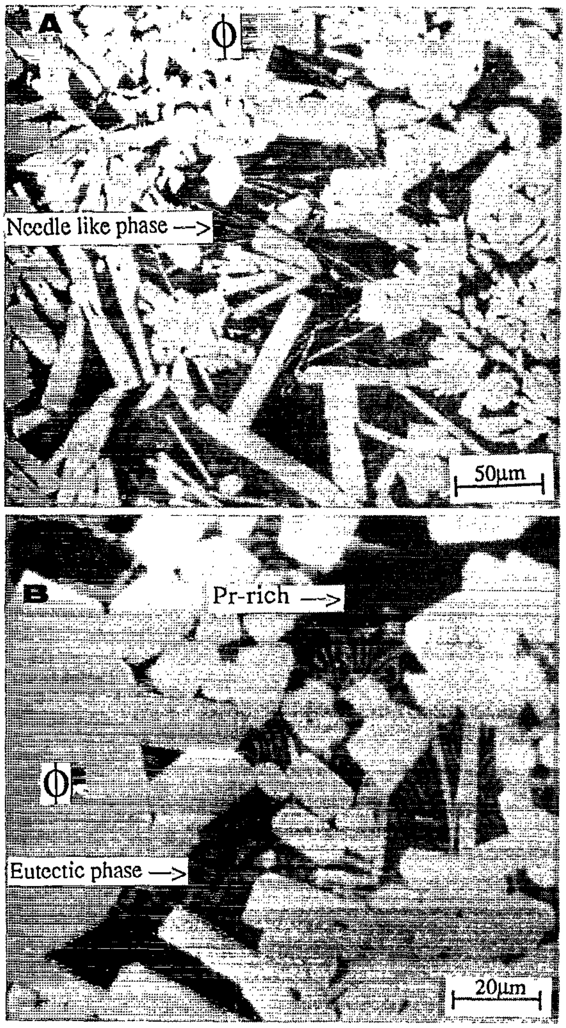

FIG. 1. Microstructure of the (A) as-cast and (B) as-cast annealed Pr-Fe-B-Cu alloy.

and the elimination of free iron. These changes are reported in more detail in Ref. 2.

Table II shows a summary of the magnetic properties found in the as-cast ingot and VFZ $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy after annealing at 1000 °C for 24 h. Before annealing, the as-cast alloy and VFZ material exhibit very poor magnetic properties. Figure 2 shows the demagnetization curves for the annealed as-cast alloys (3 and 0.7 cm molds, measured perpendicular to the largest mold wall, i.e., perpendicular to the growth direction) and VFZ material

TABLE II. Magnetic properties of as-cast and zoned Pr-Fe-B-Cu after annealing at 1000 °C for 24 h.

Growth rate (cm/h) Mold thickness	B_r (mT)	${}_iH_c$ (kA/m)	BH_{max} (kJ/m^3)
As-cast (0.7 cm)	722	600	98
As-cast (3 cm)	525	983	47
VFZ 38.10 cm/h	362	270	14
VFZ 6.35 cm/h	229	23	<1
VFZ 2.54 cm/h	97	25	<1

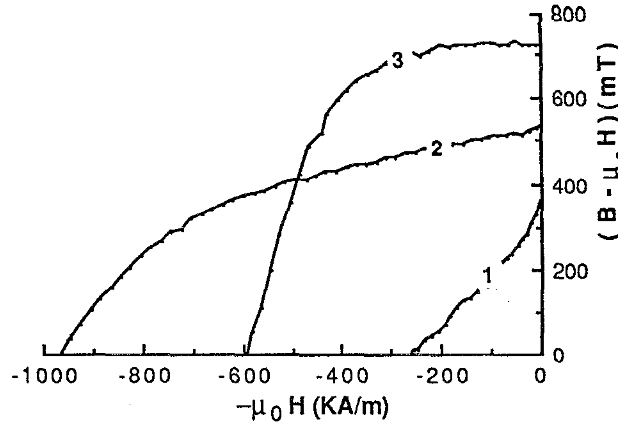

FIG. 2. Demagnetization curves for $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_{1.5}$ cast magnets and VFZ material (annealed 1000 °C 24 h). Curve 1 for VFZ material (38.1 cm/h), curve 2 for as-cast ingot, 3 cm mold and, curve 3 for as-cast, 0.7 cm mold.

(38.1 cm/h, measured perpendicular to the zoning direction). As can be seen, the solidification conditions have a dramatic effect on the B_r and ${}_iH_c$. The intrinsic coercivity of the sample cast in the 3 cm mold is much higher than that of the cast in the 0.7 cm mold, and the latter exhibits a square loop with enhanced values of the B_r and $(BH)_{max}$. These observations are consistent with an increased *c*-axis alignment in the latter and the more isotropic nature of the former.[7]

The cast alloy, which solidified under high values of growth rate *R* and thermal gradient *G* (small chill copper mold), exhibits the best magnetic properties and this suggests that, for the VFZ alloy, the zoning speed must be high in order to achieve good magnetic properties; at the growth rate of 38.1 cm/h the microstructure of the VFZ alloy shows large columnarlike grains whereas at rates of 6.35 and 2.54 cm/h the grains are large and equiaxed. Increasing growth rates of vertical float zoning lead to increasingly finer microstructures, which should produce improved magnetic properties, but this also requires increasing rates of heat removal to maintain the high values of the

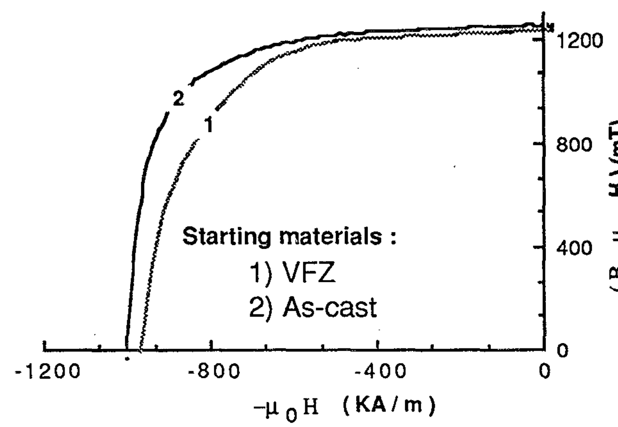

FIG. 3. Demagnetization curves for $Nd_{16}Fe_{76}B_8$ HD sintered magnets prepared from as-cast alloy and VFZ material.

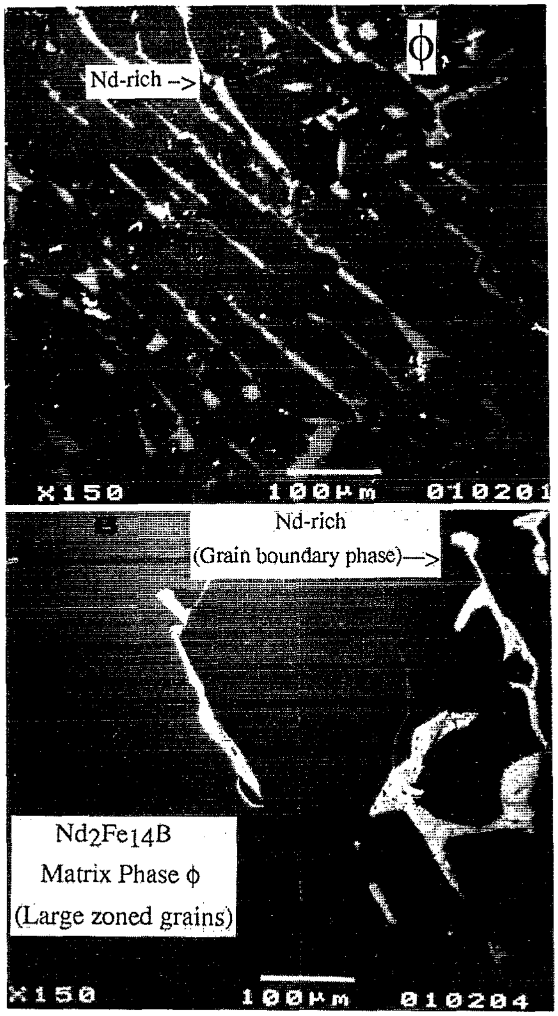

FIG. 4. Microstructure of the (A) as-cast ingot and (B) VFZ NdFeB alloy.

G/R ratio. Heat must also be removed fast enough so that the solid-liquid interface remains within the rf coil; if this is not accomplished, solidification takes place radially inwards below the rf coil and the desired preferred orientation will not be obtained. Our observations indicate that the rate of heat removal on VFZ is the major limiting experimental factor. Fu *et al.*[8] solved this problem using the directional solidification technology with liquid-metal cooling (DSTLMC) and produced Sm-Ce-Fe-Co-Zr-Cu permanent magnets (long fibers having length/diameter ratio of 100, using $G = 200$–$300\,°C/cm$ and $R = 0.005$–4 cm/min) with good magnetic properties.

B. Effect of starting microstructure on the magnetic properties of Nd-Fe-B HD sintered magnets

Figure 3 shows the demagnetization curves of $Nd_{16}Fe_{76}B_8$ HD sintered magnets prepared from the as-cast ingot ($20\times10\times3$ cm mold) and VFZ materials (2.54 cm h^{-1}), and Fig. 4 shows the respective microstructures of the start materials. Somewhat inferior magnetic properties are obtained in the case of the VFZ material, which could be due to the change in the amount and distribution of the Nd-rich material. The shape of the curve (squareness factor) seems to be the most affected. Taylor and Ward[9] have reported similar behavior in $Nd_{15}Fe_{77}B_8$ magnets by changing the cooling rate of the ingots and consequently the grain size. Lemaire *et al.*[10] characterized the inhomogeneities of macrostructure of different parts from one ingot and reported that, although the milling step could have a homogenization effect, such differences could affect the final magnetic properties of the sintered magnet. Figure 3 confirms that these differences can have some effect on the magnetic properties of sintered magnets.

IV. CONCLUSIONS

The Pr-Fe-B-Cu alloy in the cast condition exhibits some coercivity which is much enhanced by annealing at 1000 °C for 24 h. Large and small chill molds have been employed and the B_r and $(BH)_{max}$ can be increased substantially by casting the alloy in very small chill molds (and subsequent annealing). The results of magnets produced by mold casting are very promising but the usefulness or otherwise of the VFZ technique still has to be proved. In the case of the Nd-Fe-B alloy the different microstructures found in the start material have a significant effect on the magnetic properties of the HD sintered magnets.

ACKNOWLEDGMENTS

Many thanks are due to the CNPq and CNEN for the provision of a research grant (R. N. Faria). Thanks are due to REP (particularly G. Mycock) for the provision of the alloys and useful discussions. Thanks are also due to the SERC, EURAM, and CEAM for the support of the general research program of which this work forms a part.

[1] T. Shimoda, K. Akioka, O. Kobayashi, and T. Yamagami, IEEE Trans. Magn. **MAG-25**, 4099 (1989).
[2] H. W. Kwon, P. Bowen, and I. R. Harris (these proceedings).
[3] J. S. Abell and I. R. Harris, IEEE Trans. Magn. **MAG-24**, 1620 (1988).
[4] I. R. Harris, J. Less-Common Met. **131**, 245 (1987).
[5] D. Fort and D. W. Jones, J. Less-Common Met. **81**, 292 (1981).
[6] D. Fort, J. Cryst. Growth **94**, 85 (1989).
[7] D. Givord, P. Tenaud, and T. Viadieu, *Concerted European Action on Magnets*, edited by I. V. Mitchell, J. M. D. Coey, D. Givord, I. R. Harris, and R. Hanitsch (Elsevier, Amsterdam, 1989).
[8] H.-z. Fu, X.-c. Liu, Z.-x. Shi, L.-y. Wang, W. Tang, C.-g. Li, and H.-d. Song, IEEE Trans. Magn. **MAG-25**, 3797 (1989).
[9] M. Ward and J. S. Taylor, *CEAM Report*, edited by I. V. Mitchell, J. M. D. Coey, D. Givord, I. R. Harris, and R. Hanitsch, (Elsevier, Amsterdam, 1989).
[10] H. Lemaire, P. Tenaud, F. Vial, and B. Labulle, J. Magn. Magn. Mater. **83**, 234 (1990).