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The effect of ingot heat treatment on the magnetic properties of Pr–Fe–B–Cu hydrogen decrepitation sintered magnets

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Abstract

The as-cast ingot microstructure of the alloy $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ has been modified by a homogenization heat treatment of 1000 °C for 24 h. For particular processing conditions, sintered magnets prepared from the homogenized alloy using the hydrogen decrepitation (HD) process exhibit superior remanence and energy product to those prepared from the as-cast ingot. The squareness factor has also been improved considerably in the magnets prepared from the homogenized alloys. This work also showed that the influence of the initial microstructure on the intrinsic coercivity of Pr–Fe–B–Cu HD sintered permanent magnets diminishes rapidly with increasing milling time and is a minimum when the coercivity reaches the maximum value of about 20 kOe.

1. Introduction

The starting microstructure of $Nd_{15}Fe_{77}B_8$ as-cast ingots has been found to play a role in the final magnetic properties of sintered magnets [1, 2]. Previous work [3] in the authors' laboratory has shown the influence of the initial microstructure on the final magnetic properties of $Nd_{16}Fe_{76}B_8$ hydrogen decrepitation (HD) sintered magnets. In these investigations [1–3] the microstructures were modified by changing the cooling rate of the ingot [1, 2] and by a vertical floating-zone technique [3], and the sintered magnets were prepared using a standard milling time. It has been shown [4, 5] that the Nd–Fe–B bulk ingot is composed of regions with different microstructures and it has been suggested [4] that this could affect the magnetic properties of the sintered magnet. It was also proposed [4] that, for Nd–Fe–B-type alloys, the powder metallurgy route might have a tendency to rehomogenize the material through the milling and sintering steps, and if this were the case then the magnet-processing steps would cause a progressive attenuation of the influence of the ingot microstructure on the magnetic properties of the sintered magnet.

It has been assumed in the present work that any rehomogenizing effects would be determined mostly by the milling stage and that a greater influence of the initial microstructure would be expected at lower milling times. Recently,

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it has been shown [6] that, even for as-crushed material with a coarse particle size, HD sintered magnets based on the alloy $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ exhibited appreciable permanent magnetic properties and this alloy exhibited appreciable permanent magnetic properties even in the cast and annealed condition [3]. Therefore, in order to investigate the detailed effect of milling time, this alloy was considered to be the most suitable candidate since the effects at low milling times can be observed. This is not possible for Nd–Fe–B alloys since they exhibit virtually no permanent magnetic properties without appreciable milling [7]. Thus the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy has been selected for this work instead of the previously studied alloys [1–2], in order to allow an investigation of a wider range of milling times.

An initial heat treatment for homogenization, usually at elevated temperature and for a few days, has been applied to Nd–Fe–B alloys [8] to eliminate free iron and composition gradients, by accelerating the solid state diffusion and consequently yielding a more homogeneous alloy. Thus, homogenization by annealing the as-cast ingot was used as a controlled means of modifying the alloy microstructure prior to magnet processing. The magnetic behaviours of magnets prepared from this homogenized alloy were compared with those of samples prepared from the standard as-cast ingot alloy. In the present work the possibility that the ingot homogenization heat treatment and milling time influence the final magnetic properties of HD sintered magnets of a $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy has been investigated.

2. Experimental details

The alloy investigated in this work has been provided by Rare Earth Products. The alloy was prepared in a rectangular (20×10×3 cm) water-cooled copper mould, and the chemical analysis of the alloy is given in Table 1. The homogenization heat treatment of the ingot was carried out under vacuum at 1000 °C for 24 h and slow cooled in the furnace (cooling rate of approximately 3.5 °C min^{-1}).

In order to produce the magnets via the HD process [9], the following procedure was adopted. Small pieces of the bulk ingot (care has been taken to choose the starting alloy only from the central uniform regions of the ingot) were placed in a stainless steel hydrogenation vessel which was evacuated to backing-pump pressure and hydrogen was then introduced to a pressure

TABLE 1

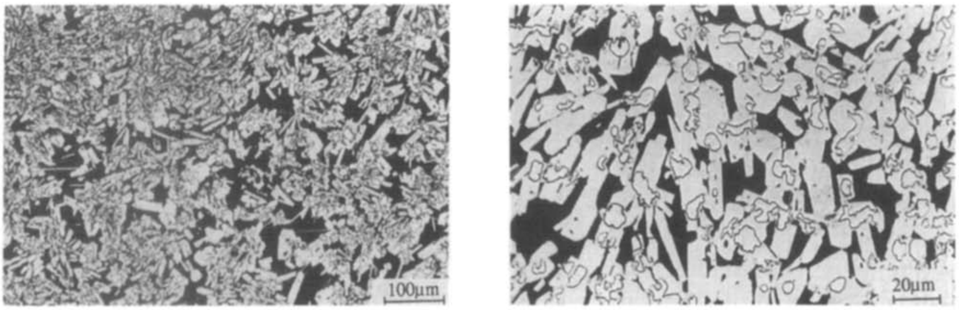
Chemical analysis of the as-cast alloy

Element	Content (at.%)	Content (wt.%)
Pr	20.5	40.0
Fe	73.8	Balance
B	3.7	0.60
Cu	2	1.60

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 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 h and furnace cooled. The as-sintered magnets then received a postsintering heat treatment [6] under vacuum at 1000 °C for 24 h (although 5–10 h was shown to be sufficient to achieve full magnetic properties [6], 24 h was used for comparison) and their magnetic properties were determined in a permeameter.

3. Results and discussion

The as-cast state of the Pr–Fe–B–Cu alloy is shown in Figs. 1(a) and 1(b) and is very heterogeneous. Phase analysis indicates that the alloy is composed of the matrix phase $Pr_2Fe_{14}B$ (platelike white crystals), copper and praseodymium-rich phases in the intercrystalline regions and free iron inside the matrix phase (consistent with the peritectic nature of this phase [10]). The $Pr_{1+\epsilon}Fe_4B_4$ boride phase has not been observed. The microstructure of the homogenized Pr–Fe–B–Cu alloy is shown in Fig. 2. A comparison with the as-cast microstructure in Fig. 1(a) demonstrates that there is no significant grain growth during the homogenization heat treatment, which is consistent with previous work [11]. The most obvious change during the heat treatment is the elimination of free iron, which can be seen in Fig. 1 but not in Fig. 2. Due to a reaction between the praseodymium-rich phase and copper a second change observed is the reduction in the amount of grain boundary needlelike phase and the appearance of a coarse grain boundary eutectic [3, 11] (not seen in the etched micrographs shown here). It has been shown [11] that a minimum of 5 h is required for this homogenization heat treatment to occur, but 24 h was used in the present work to avoid any possible variations due to the homogenization procedure.



(a) (b)

Fig. 1. Optical micrographs showing (a) a general view and (b) details of the microstructure of the as-cast $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy (etched with Nital). Free iron can be observed within each $Pr_2Fe_{14}B$ crystal.

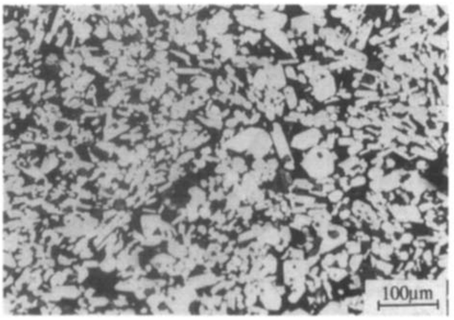


Fig. 2. Optical micrograph showing a general view of the microstructure of the homogenized $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy (etched with Nital). There is now no evidence of free iron within the $Pr_2Fe_{14}B$ crystals.

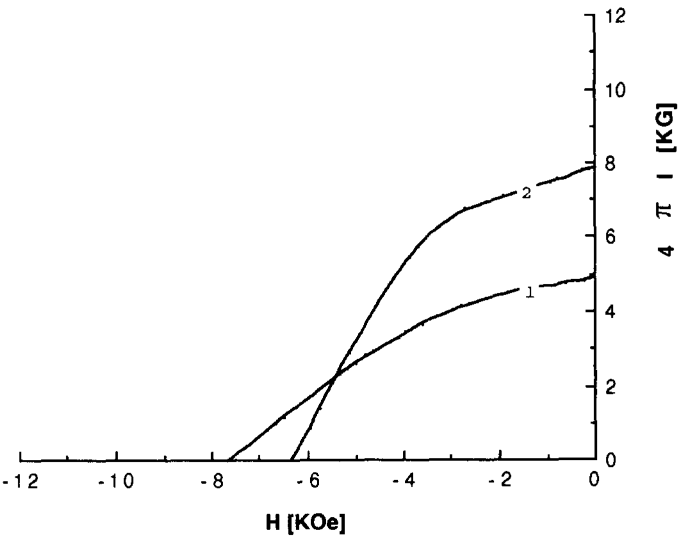


Fig. 3. Demagnetization curves for $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnets prepared using the crushed alloy: curve 1, as cast; curve 2, homogenized.

Figure 3 shows the demagnetization curves for HD magnets prepared using the as-cast and homogenized alloy crushed with a pestle and mortar and then sintered. There is a dramatic increase in remanence and consequently in energy product for the magnets made from the homogenized alloy. This can be attributed to the better density (see Table 2) and to the better loop shape, which can be attributed to the elimination of the free iron (magnetically soft phase) from the ingot material and to improved alignment. These magnets exhibit appreciable hard magnetic properties, whereas $Nd_{16}Fe_{77.5}B_{6.5}$ magnets prepared under the same conditions [7] exhibit virtually no hard magnetic properties. This difference in behaviour can be attributed to (a) the much finer microstructure of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy in the as-cast state (achieved

TABLE 2

Density and magnetic properties of magnets prepared from as-cast and homogenized alloy[a]

Property[b]	Value		
	Crushed	4 h milling	9 h milling
ρ^*/ρ	7.14/6.48	7.37/7.32	7.32/7.33
$BH_{\max}^*/BH_{\max}$	11.0/4.9	27.6/22.7	25.4/24.9
B_r^*/B_r	7.8/4.9	10.9/10.0	10.1/10.7
${}_iH_c^*/{}_iH_c$	6.4/7.7	9.1/10.2	20.2/19.7
SF*/SF	0.33/0.30	0.73/0.60	0.59/0.39

[a] ρ^*, $BH_{\max}^*$, B_r^*, ${}_iH_c^*$ and SF* are the values for the homogenized material.
[b] ρ is in grams per cubic centimetre, $BH_{\max}$ in megagauss oersteds, B_r in kilogauss, ${}_iH_c$ in kilo-oersteds and SF is a dimensionless ratio.

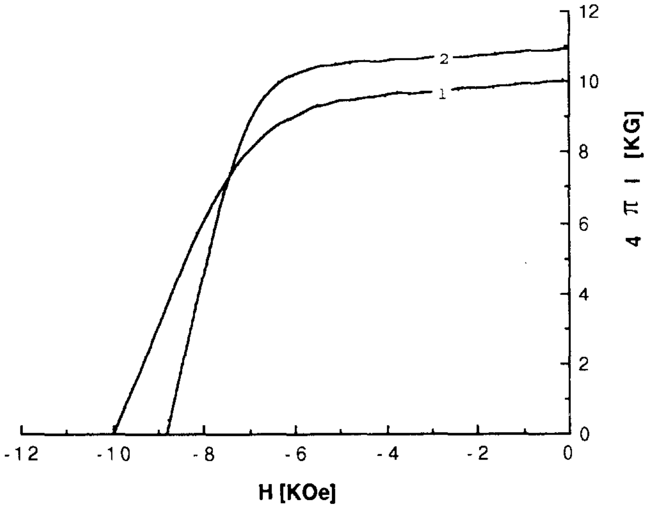


Fig. 4. Demagnetization curves for $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnets produced using the alloy milled for 4 h: curve 1, as cast; curve 2, homogenized.

with the reduced boron content and copper substitution [12]), (b) the extensive amount of praseodymium-rich material surrounding each $Pr_2Fe_{14}B$ crystal and (c) the enhanced anisotropy field of the matrix $Pr_2Fe_{14}B$ phase [13] compared with that of $Nd_2Fe_{14}B$.

The demagnetization curves for magnets produced using the as-cast and homogenized alloy ball milled for 4 h are shown in Fig. 4. The improvement in energy product for the magnet prepared from the homogenized alloy is still very significant. It can also be noticed that the intrinsic coercivity of the magnet made from the as-cast alloy is again higher than that of the magnet made from the homogenized alloy and the latter exhibits a squarer loop with enhanced values of the remanence. Recent studies in Pr–Fe–B sintered magnets [14] have shown that an improved grain alignment leads to a reduction of coercivity due to an increase of internal demagnetizing fields, which is consistent with the present observations. The same behaviour has also been reported for the Nd–Fe–B sintered magnets [15]. Full density has been achieved for both magnets with this milling time (see Table 2). Figures 5 and 6 show the typical microstructures of the magnets prepared from the as-cast and homogenized alloys milled for 4 h. The uniform distribution of the praseodymium-rich material can be seen in both magnets. The magnet prepared from the homogenized alloy exhibits a somewhat bigger grain size, which could be another contributory factor to the decrease in coercivity for the magnets prepared from the homogenized alloy.

The demagnetization curves for magnets produced using the as-cast and homogenized alloy ball milled for 9 h are shown in Fig. 7. High coercivity was achieved with this milling time after the postsintering heat treatment for the magnets prepared from both the as-cast and homogenized alloy, which is consistent with previous studies [6]. The homogenization heat treatment improves the squareness factor, which enhances the energy product, but the remanence and density are slightly reduced. The two curves are much closer to each other than in the previous case. This behaviour indicates that full magnetic properties are obtained in both types of magnets with this milling time. It has been shown [16] for $Nd_{16}Fe_{76}B_8$ HD magnets that full magnetic properties are achieved using milling times of 18–24 h (roller ball milling). Much shorter milling times (9 h) are required for the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy and this can be attributed to the greater amount of rare-earth-rich material in this alloy and to the higher anisotropy field of $Pr_2Fe_{14}B$ [13].

The above observations are summarized in the percentage change in the magnetic properties achieved by the homogenization heat treatment given in Table 3. 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

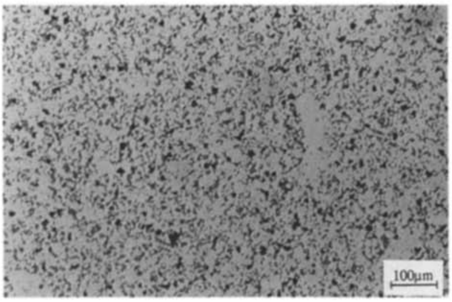


Fig. 5. Optical micrograph showing the microstructure of the magnet prepared from as-cast $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy milled for 4 h.

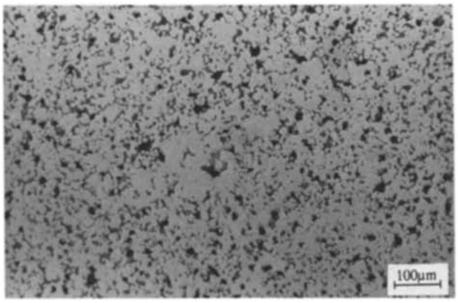


Fig. 6. Optical micrograph showing the microstructure of the magnet prepared from homogenized $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy milled for 4 h.

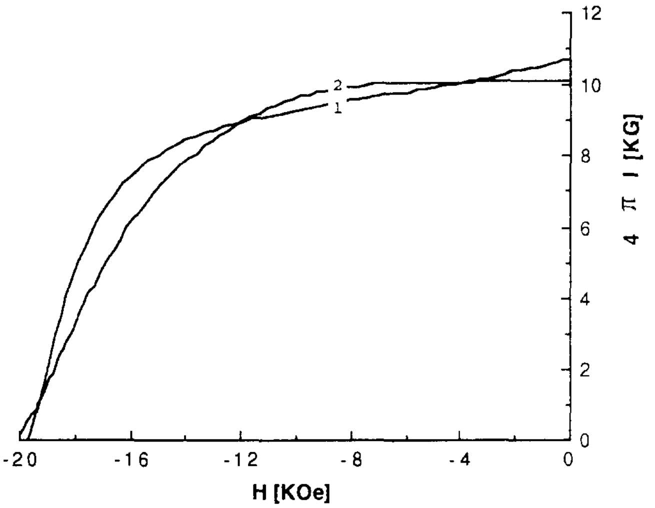


Fig. 7. Demagnetization curves for $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ HD magnets prepared using alloys milled for 9 h; curve 1, as cast; curve 2, homogenized.

TABLE 3

Percentage variation in the magnetic properties of magnets prepared from as-cast and homogenized alloy[a]

Property	Variation (%)		
	Crushed	4 h milling	9 h milling
ΔBH_{max}	124.5	21.6	2.0
ΔB_r	59.2	9.0	−5.6
$\Delta_i H_c$	−16.9	−10.8	2.5
ΔSF	10.0	21.7	51.3

[a] 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.

progressive milling time and the percentage change in energy product, remanence and intrinsic coercivity becomes very small around 9 h of milling time. Thus the present observations on the alloy $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ indicate 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 postsintering 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.

4. Conclusions

$Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ 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 9 h. This behaviour can be attributed to the rehomogenization of the cast structure after milling for the extended period and then sintering. Further studies are being carried out to optimize the procedures outlined in this paper and to correlate the magnetic behaviour with the detailed microstructure.

Acknowledgments

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