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The influence of free iron on the hydrogen decrepitation capability of some Nd(Pr)–Fe–B alloys

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Abstract

Hydrogen decrepitation (HD) followed by jet-milling is now well established as an economic and convenient powder preparation route for the production of sintered Nd–Fe–B based magnets. However, there is often residue in the H-decrepitated and milled material due to the presence of α-iron in the microstructure of the as-cast alloys. The residue is separated from the rest of the material by sieving the powder in order to attain a powder with a suitable average particle size. Thus, the extent of this residue has an overall impact on the total cost of a sintered magnet and it could also affect the final composition of the sintered magnets. In this paper, the influence of α-iron on the amount of the residue in the H-decrepitated and roller milled powder in some Nd(Pr)–Fe–B based alloys has been investigated. The ductile free iron, particularly in the form of large dendrites, was found to act as an obstacle to the propagation of micro-cracks generated by the HD process and was therefore the main cause of the residue. Investigation of a number of as-cast Nd–Fe–B alloys revealed that, with increasing Nd content in these alloys, the size and amount of the α-iron in the as-cast state was reduced. This resulted in a pronounced reduction in the amount of the residue after a standard HD and milling process. In a $Nd_{13}Fe_{80.5}B_{6.5}$ or a $Pr_{16.9}Fe_{79.1}B_4$-type alloy, the amount of residue was found to be considerable after the standard HD and milling treatment. Homogenising the alloys at 1050°C for different times resulted in the eventual disappearance of the residue after the standard HD and milling treatment. All the residues were found to be very stable in air at room temperature, but producing a clean polished surface in any of these particles, even under dry conditions, resulted in much increased reactivity. Possible means of avoiding α-Fe in the initial alloys have also been explored.

Keywords: NdFeB alloys; Permanent magnet materials; Hydrogen decrepitation

1. Introduction

Soon after the discovery of Nd–Fe–B magnets in 1984 [1,2], hydrogen decrepitation (HD) at room temperature followed by milling was announced as an effective route of powder preparation for this material [3–5]. Since then, HD and subsequent roller milling has been used successfully in the production of Nd(Pr)–Fe–B based sintered magnets in the Applied Alloy Chemistry Group (AACG) Laboratories in the School of Metallurgy and Materials, University of Birmingham. The hard magnetic phase in these compounds, i.e. Φ ($Nd_2Fe_{14}B_1$ or $Pr_2Fe_{14}B_1$) forms by a pseudobinary peritectic reaction of $L+\gamma\text{-Fe}=\Phi$ [6–8] and this means that ingots with these compositions, cast and slowly cooled, will contain an appreciable amount of free iron dendrites. Since, in recent years there has been a tendency in the Nd–Fe–B based alloys to move towards the stoichiometric composition in order to increase the $(BH)_{\max}$ values of the magnets to around 400 kJ m^{-3} [9–12], it seems that the occurrence of α-iron in the cast structures of most of these alloys would be inevitable. When the amount of free iron is considerable and the size of the α-iron dendrites is large enough, then a substantial amount of residue is produced after a standard HD and milling treatment. The extent of this residue will have an overall impact on the total cost of a sintered magnet and it could also affect the final composition.

Thus, the present work was undertaken in order to investigate the influence of free iron on the amount of residue in the H-decrepitated and roller milled powder in some Nd(Pr)–Fe–B based alloys. In addition, a number of

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possible means of avoiding free iron in the microstructure of the cast alloys have been discussed.

2. Materials and experimental procedure

The nominal compositions of the alloys [supplied by Rare Earth Products Ltd. (UK)] investigated in this work, are summarised in Table 1. The bulk ingots were broken up into smaller pieces of around 1–2 cm^3 and then 50 g from each material hydrogenated inside an evacuated hydrogen vessel at a pressure of just over 2 bar at room temperature. After the HD process, the powders were transferred in a nitrogen glove box, to a cylindrical milling pot filled to around half of its volume with carbon chromium steel balls and then roller milled under cyclohexane for 20 h. Prior to sieving, the milled powders were dried under a rotary vacuum in the glove box. Three sets of sieves with mesh numbers of 40, 60 and 100 respectively were then employed to sieve the powder. The residues with an average particle size of around 3 mm were almost completely separated from the rest of the powders in the first sieve (40 mesh).

The residue weight (r) to the total weight (t=50 g) ratio (r/t) was then identified for three specimens of each alloy and the mean value was used to identify the HD capability for each alloy on a % basis. In the case of alloys A and G with the highest r/t ratios and thus the lowest HD capability within the alloys studied in this work, homogenising treatments of 1050°C for 4 to 24 h were applied in order to remove a major part of the free iron, and the effect of this treatment on the r/t ratio was investigated.

The residues were very stable in air at room temperature. However, producing a clean polished surface in any of these particles, even under dry conditions, resulted in an increased reactivity which led to an eventual explosion of the particles into many small pieces. This can be attributed to the reaction of the residues with oxygen through the clean polished surfaces. Therefore, particular care had to be taken in the preparation of the microscopic specimens of the residues. These specimens had to be examined promptly after mounting, otherwise both the residues and the mounting material eventually disintegrated.

Table 1
Nominal compositions of the initial alloys (indicated as alloys A, B, C, D, E, F and G) and the mean volume fraction of α-iron in their cast structure

Alloy	Composition	vol. % α-Fe
A	$Nd_{13}Fe_{80.5}B_{6.5}$	24.95±4.36
B	$Nd_{13.5}Fe_{79.75}B_{6.75}$	15.79±3.52
C	$Nd_{14}Fe_{79}B_7$	8.25±3.12
D	$Nd_{15}Fe_{77.3}B_{7.7}$	3.65±1.75
E	$Nd_{16}Fe_{76}B_8$	0.00
F	$Nd_{13}Fe_{78}NbCoB_7$	1.27±0.56
G	$Pr_{16.9}Fe_{79.1}B_4$	28.78±4.79

The microstructures of the cast ingots and residues were investigated by polishing sections and examining in a JSM 6300 JEOL scanning electron microscope (SEM) with electron probe microanalysis (EPMA) facilities using backscattering electron imaging. The volume fraction (vol. %) of α-Fe in the specimens was identified by means of a computerised image analyser and for this, at least four back-scattered electron image micrographs, taken at random positions over the whole specimen, were used and the mean values were then selected as the vol. % of α-Fe.

3. Results and discussion

The backscattered electron image of the cast specimens of alloys A, B, C, D, E, F, and G are shown in Fig. 1 ((a), (b), (c), (d), (e), (f) and (g)), respectively. EPMA using energy dispersive X-ray analysis (EDX), indicated a non-homogenous Nd(Pr)-rich intergranular phase with an overall composition of $[Nd(Pr)]_{60\text{-}90}Fe_{40\text{-}10}$ together with a 1:4:4-type boride phase ($Nd_1Fe_4B_4$; no boride phase was observed in alloy G) distributed between a 2:14:1-type matrix phase $\{[Nd(Pr)]_2Fe_{14}B_1\}$. Islands of α-iron dendrites were observed within the 2:14:1-type grains in most of these specimens. In Table 1, the mean vol. % of α-Fe are summarised and these values together with Fig. 1(a) through (e), indicate that, as expected, the proportion and size of α-iron dendrites were reduced dramatically when the Nd content in the alloys increased from 13 at. % in alloy A to 16 at. % in alloy E, such that in alloy E, no α-iron was identified (Fig. 1(e) and Table 1). Very small amounts of α-iron were observed in the cast specimen of alloy F (Fig. 1(f) and Table 1) and this confirms the results obtained by previous workers [13] who found a substantial reduction in the amount of α-iron by addition of Nb to the stoichiometric Nd–Fe–B alloys. The amount of α-iron in the cast specimen of this alloy has been reported to be 0.98±0.5 vol. % using image analysis measurements [14] which is in good agreement with the present work. Substantial amounts of α-iron were observed in the cast specimen of alloy G (Fig. 1(g) and Table 1).

The backscattered electron image of the specimens prepared from the residues of alloys A and G (which had the highest proportions of α-iron within the alloys investigated in this work) are shown in Fig. 2(a) and (b), respectively. A predominant part of the microstructures of these specimens consists of large dendrites of α-iron which are ductile in nature. Mean vol. % of α-iron in the residues (Table 2) is considerably greater than that of the corresponding cast specimens (see Table 1). Thus, the propagation of microcracks, initiated by the HD process in both the 2:14:1 grains and Nd-rich (Fig. 2(a)) or Pr-rich (Fig. 2(b)) regions, were effectively stopped by the large α-iron dendrites which were therefore the main cause of the residue formed after a standard HD and milling process.

The values of r/t %, after a standard HD and roller

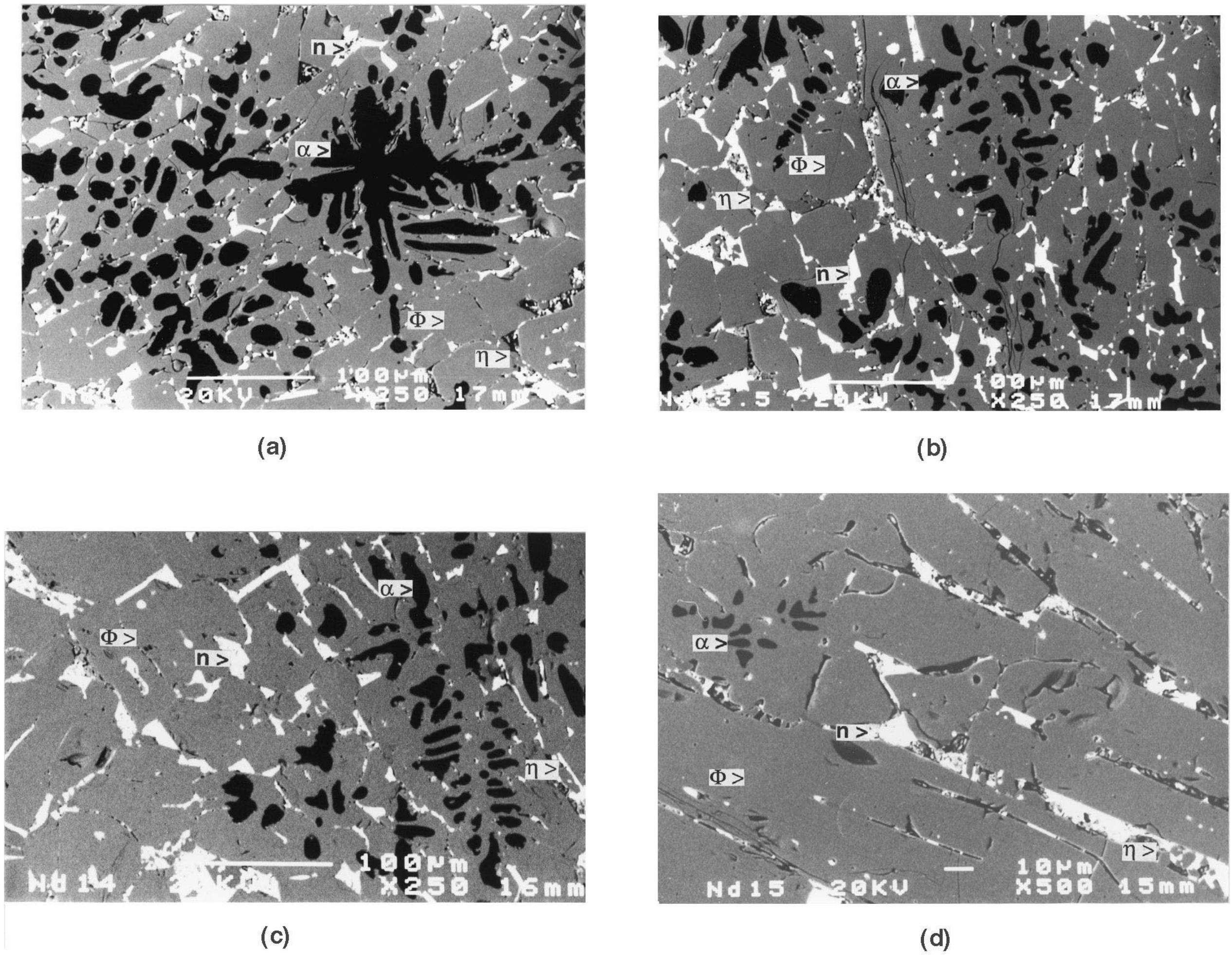

Fig. 1. Backscattered electron images of the cast specimens of (a) alloy A, (b) alloy B, (c) alloy C, (d) alloy D, (e) alloy E, (f) alloy F, and (g) alloy G. (n or p) Nd-rich or Pr-rich intergranular region, (Φ) 2:14:1-type matrix phase, (η) 1:4:4-type boride phase, and (α) free α-iron.

milling process, are listed in Table 3. The highest r/t % belongs to alloys A and G with the corresponding lowest HD capability values and highest α-iron contents (see Table 1). H-decrepitated and milled specimens of alloy E with no α-iron, and alloy F with a negligible amount of α-iron (Table 1), did not show any residues and thus both exhibit a 100% HD capability. Plots of the variations in the r/t % versus at. % Nd (Fig. 3) or versus vol. % α-iron (Fig. 4) in the cast specimens of alloys A, B, C, D and E indicate a regular relationship between the r/t % and the Nd or α-Fe content with the disappearance of the residue between 15 and 16 at. % Nd[1] with corresponding averages of vol. % α-iron of 3.65 to 0 respectively. This is consistent with the microstructures of these alloys (see Fig. 1(d) and (e)). The non-linear relationship between r/t % and vol. % α-iron (Fig. 4) probably indicates that the amount of residue also depends on the scale of the α-iron dendrites as well as on the overall amount. The variation in the α-iron content with at. % Nd in the cast specimens of alloys A to E is shown in Fig. 5. There is a marked reduction in the amount of α-iron with increasing at. % Nd in these alloys and the vol. % of α-iron is reduced to 0 at 16 at. % Nd.

Variations in the r/t % versus homogenisation time at 1050°C in specimens of alloys A and G are compared in Fig. 6. Homogenising specimens of alloys A and G for up to 24 h, at successive time intervals of 4 h, resulted in the eventual disappearance of the residues (after the standard HD and milling), after 12 and 20 h of homogenising, respectively. This could also be considered as further evidence that the diffusion rate in Pr–Fe–B alloys is rather slower than that of Nd–Fe–B alloys under identical conditions as reported by Neiva et al. [8].

The microstructure of a specimen of alloy A homogenised at 1050°C for 12 h and that of a specimen of alloy G homogenised at the same temperature for 20 h are shown in Figs. 7 and 8, respectively. It can be seen that there is still a small amount of α-iron left in the central parts of

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[1] These are nominal compositions and make no allowance for the loss of metallic Nd due to oxidation during alloy preparation or during the milling operation.

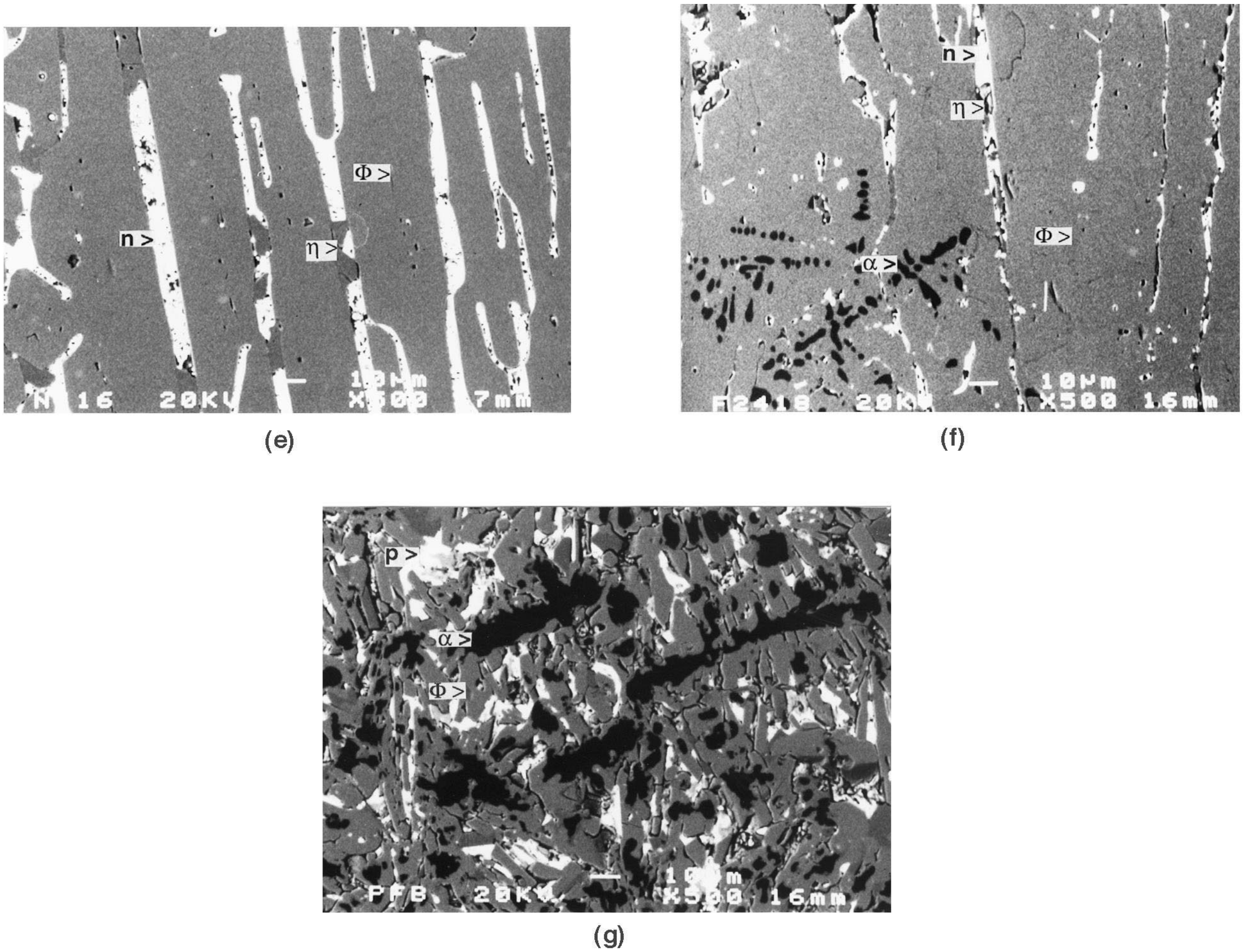


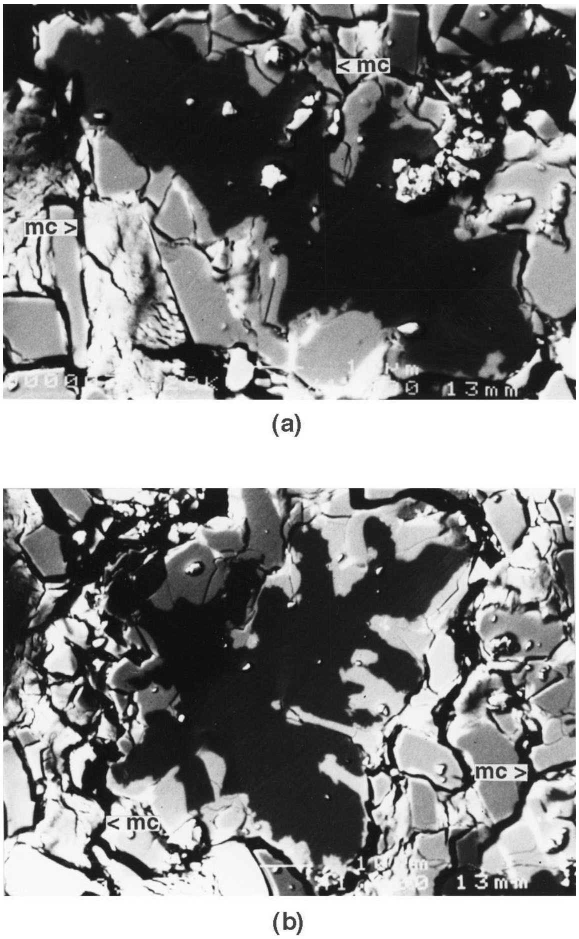
Fig. 1. (*continued*)

those grains which were identified, as a Nd(Pr): Fe, 2:17-type phase. This indicates that the dissolution of α-iron within the 2:14:1-type matrix results in the formation of an intermediate 2:17-type phase. This is in agreement with previous observations in the authors' laboratory [15]. Unlike α-iron, the brittle 2:17-type phase, even in the form of relatively large grains, does not appear to influence the amount of residue. However, as a magnetically soft phase it would adversely influence the magnetic properties, if it occurred in the sintered magnet.

4. Possible measures to reduce residues

The present study demonstrates clearly the undesirable effect of free iron on the HD capability of the Nd(Pr)–Fe–B based cast alloys. There is often a considerable amount of residue ($>$15 wt. %), after a standard HD and milling process, due to the presence of α-iron in the microstructure of most of the as-cast alloys studied in this work. Since the residue will increase the cost of a sintered magnet and could also affect its final composition, it would be a significant advantage to avoid α-iron in the initial material. Some possible methods of avoiding α-iron in the microstructure of the initial alloys can be summarised as follows:

1. Compositional adjustment: Since in the Nd(Pr)–Fe–B based cast alloys the hard magnetic 2:14:1-type (Φ) phase is formed by a peritectic reaction between the liquid phase (L) and α-iron, it is possible (as in alloy E), by a proper adjustment of the compositions of the alloys, to avoid the peritectic reaction and thus produce α-iron free ingots. However, this necessitates Nd(Pr)-rich compositions and this is against recent trends where the compositions in the Nd–Fe–B alloys are moving towards the stoichiometric composition in order to increase the $(BH)_{\max}$ values.
2. Additives: Additions of, for example, Nb to stoichiometric or near stoichiometric Nd–Fe–B alloys (as in alloy F) reduces very effectively the amount of α-iron dendrites [13,15]. This could be used as a practical means of avoiding α-iron, providing the additions do not have an adverse effect on the permanent magnetic properties of the sintered magnets.
3. Rapid cooling: Rapid cooling of the cast alloys, in



(a)

(b)

Fig. 2. Backscattered electron images of the specimens prepared from the residues of (a) alloy A and (b) alloy G. The microcracks (mc) initiated in the Nd(Pr)-rich regions and the 2:14:1-type matrix can be seen in both of the micrographs.

Table 2
Mean volume fraction of α-iron in the residue specimens of alloys A and G

Residue	vol. % α-Fe
Alloy A	37.9±6.86
Alloy B	40.25±3.23

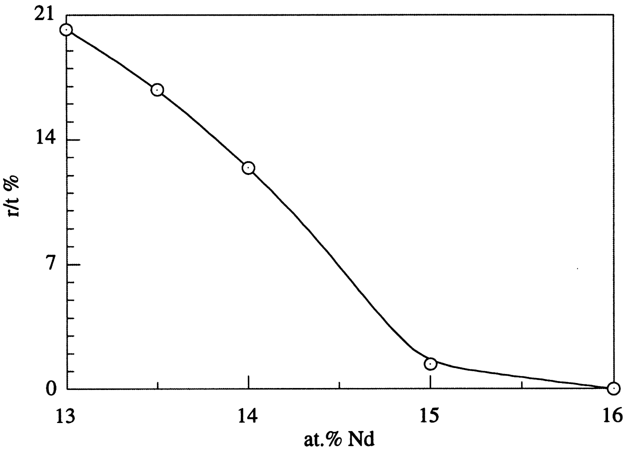


Fig. 3. Variations in the r/t % with Nd content in the Nd–Fe–B alloys.

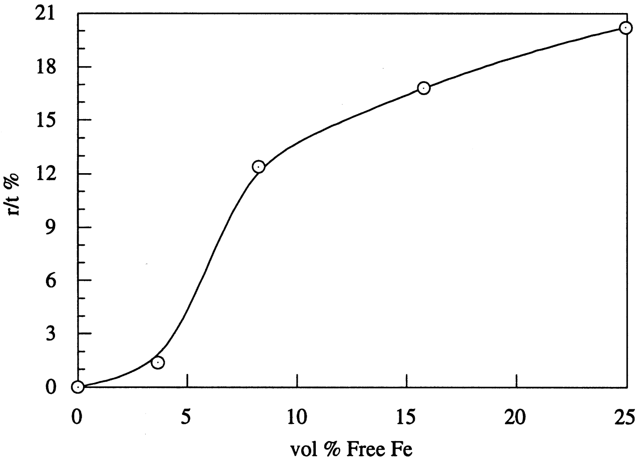


Fig. 4. Variations in the r/t % with α-iron content in the Nd–Fe–B alloys.

particular in the region of the peritectic reaction (as in book mould casting or spread casting on a copper mould with no boundary and possibly with water cooling facilities) reduces the proportion and scale of the α-iron [16].

4. Homogenising treatment: Homogenising the cast ingots at a suitable temperature for a long time, will reduce the proportion and scale of the α-iron dendrites (as in alloys A and G after homogenising at 1050°C). However, this is probably not a practical option because of the time and energy consumed.

Table 3
The r/t % in the specimens of alloys A, B, C, D, E, F and G after the standard HD and roller milling treatment

Alloy	A			B			C			D			E			F			G		
NO.	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
r/t %	17.9	24.5	18.2	15.2	17.4	17.8	10.7	13.4	13.1	1.2	1.9	1.1	0	0	0	0	0	0	21.5	27.7	23.7
Mean (r/t)%	20.2			16.8			12.4			1.4			0			0			24.3		
HD Cap. (%)	79.8			83.2			87.6			98.6			100			100			75.7		

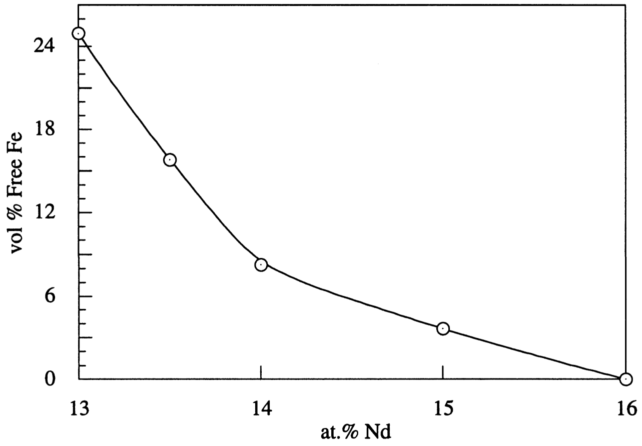


Fig. 5. Variations in the vol. % α-iron with at. % Nd in the Nd–Fe–B alloys.

5. Hydrogen-disproportionation-desorption-recombination (HDDR) process: The HDDR process has been reported as an effective route for eliminating [17] or reducing [15] the amount of α-iron. It has been shown that the HDDR process homogenises the alloy at a relatively low temperature (800°C) and over a relatively short period of time (around 1 h) compared to that of a standard homogenisation treatment [15]. However, it will be necessary to grow the grains to ensure that, after milling, the powder consists of single crystal particles.

5. Conclusions

The present work has shown that free iron has a very deleterious effect on the HD capability of the Nd(Pr)–Fe–B based alloys. Eliminating or at least reducing the proportion and scale of the α-iron, particularly in stoichiometric or near stoichiometric Nd–Fe–B alloys is, therefore, of great practical interest. These alloys, under normal casting conditions, usually contain a considerable amount of free iron. From a practical point of view, it seems that adding a suitable element(s) to the Nd(Pr?)–Fe–B alloys and utilising a modified casting technique, such as water cooled book moulding or spread casting on a water cooled copper plate with no boundaries, would effectively suppress the α-iron dendrites in the initial cast alloys. This would result in residue-free powder after the HD and milling treatment which would reduce the cost of a sintered magnet and allow close control of the final composition.

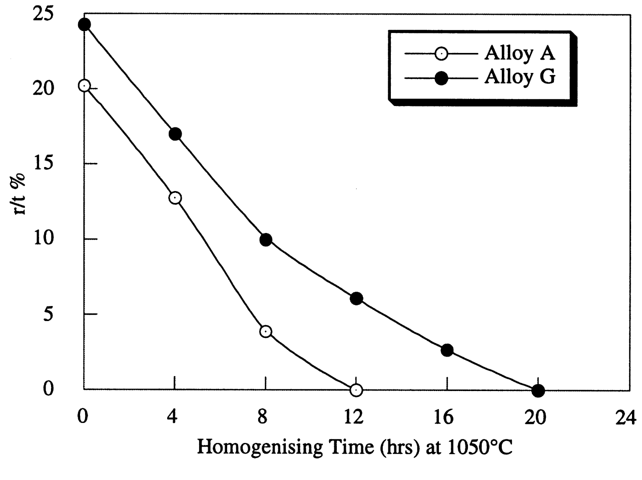


Fig. 6. Variations in the r/t % in the specimens of alloys A and G with homogenising treatment time (at 1050°C).

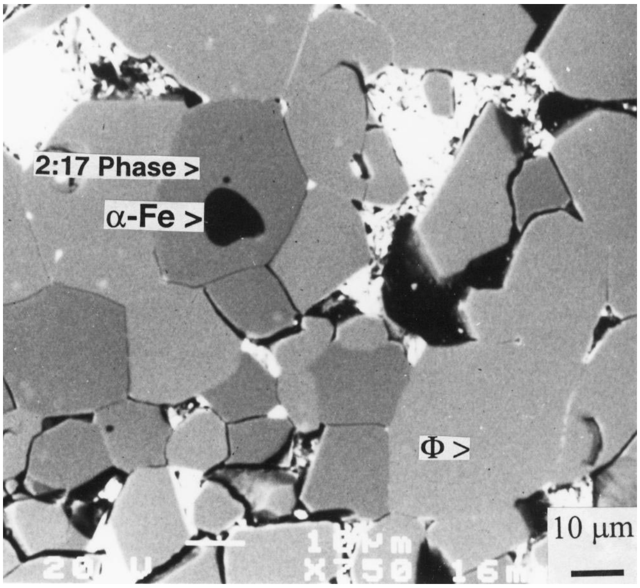


Fig. 7. Backscattered electron image of a specimen of alloy A homogenised at 1050°C for 12 h.

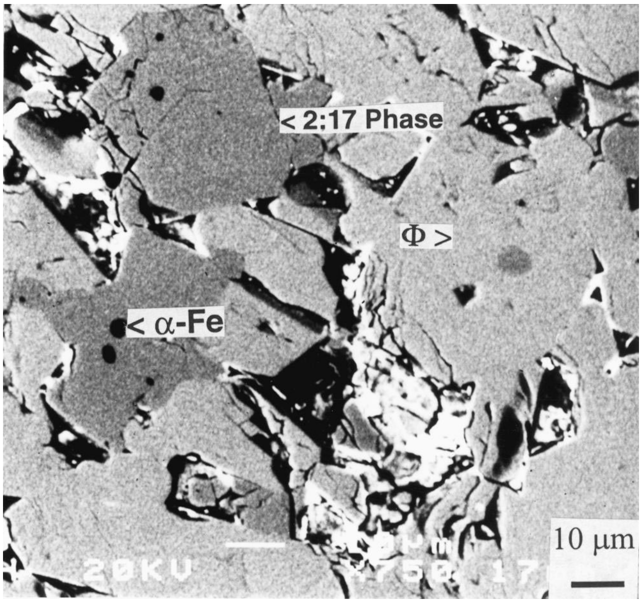


Fig. 8. Backscattered electron image of a specimen of alloy G homogenised at 1050°C for 20 h.

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