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The effect of the cooling rate on the intrinsic coercivity of some Nd–Fe–B based permanent magnets

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Abstract

The effects of furnace cooling, air cooling and quenching in liquid argon from 1100 °C on the coercivity of $Nd_{16.4}Fe_{75.7}B_{7.9}$ (A), $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ (B) and $Nd_{17}Fe_{79}B_4$ (C) sintered magnets have been investigated. In magnet A, a considerable fall in H_{ci} occurred on quenching whilst air or furnace cooling caused successively less deterioration in H_{ci}. The coercivity of quenched magnet A was partially restored during annealing at 600 or 680 °C. In magnet B, no significant fall in H_{ci} was observed on cooling at different cooling rates, and a considerable improvement in H_{ci} occurred on subsequent annealing at 600 °C. Magnet C showed a remarkable increase in H_{ci} on quenching whilst air cooling or furnace cooling resulted in successively smaller improvements in the H_{ci} values. The coercivity of magnet C dropped drastically after quenching and then annealing at 600 °C. In magnets A and B the coercivity behaviour on cooling was related mainly to the melting temperature and to the wettability characteristics of the intergranular phase(s) in these magnets, and to the formation of metastable phases on quenching, whereas in magnet C, redistribution and dissolution of soft magnetic phase(s) during the high temperature (1100 °C) treatment could be responsible for the changes in H_{ci}.

1. Introduction

The cooling rate after sintering [1, 2] or after a high temperature (1100 °C) solid solution treatment [3–5] has been shown to have a definite influence on the intrinsic coercivity and energy product of Nd–Fe–B based sintered magnets. With increasing cooling rate, an increased deterioration in intrinsic coercivity and energy product has been reported [1–5]. This behaviour has been related to a combination of increased numbers of intergranular quenching cracks, local strains at grain boundaries and phase interfaces [1], changes in the constitution of the grain boundaries [4] and progressively less wettability of the intergranular phase(s) with increasing cooling rates [5]. One of the other reported effects of rapid cooling or quenching is that these introduce atomic scale roughness between the grains and grain boundaries, which increases the local self-demagnetizing field and reduces the intrinsic coercivity [6, 7].

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In recent model investigations [8–10], using alloys with compositions similar to that of the neodymium-rich intergranular region in Nd–Fe–B sintered magnets, two types of ferromagnetic phases known as A_1 and A′ with an identical Curie temperature of 245 °C have been identified. It has been shown that these phases are present within intergranular regions of slowly or rapidly cooled magnets; however, their volume fraction was reported to be much higher in rapidly cooled sintered magnets. The lower H_{ci} value in quenched magnets has been attributed to the larger volume fraction of these phases which are magnetically softer than the $Nd_2Fe_{14}B_1$ phase [9].

The present work was undertaken to examine the effects of the rate of cooling from 1100 °C upon the intrinsic coercivity in $Nd_{16.4}Fe_{75.7}B_{7.9}$ (A), $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ (B) and $Nd_{17}Fe_{79}B_4$ (C) sintered magnets, and some possible reasons for the observed behaviour are given. A is close to the standard composition for sintered magnets; B and C are the compositions investigated previously in this laboratory [11]. The effects of subsequent annealing at 600–680 °C (magnet A) or 600 °C (magnets B and C) on the magnetic properties of the quenched magnets have also been investigated.

2. Experimental procedure

The commercial grade magnet with a nominal composition of $Nd_{16.4}Fe_{75.7}B_{7.9}$ (magnet A) was supplied by Philips Components Ltd. (UK). The sintered magnets with nominal compositions of $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ (magnet B) and $Nd_{17}Fe_{79}B_4$ (magnet C) were processed in this laboratory and details of the production procedure have been given elsewhere [11]. The alloys for both of the above magnets were supplied by Rare Earth Products Ltd. (UK).

In each experiment, three magnets of one of these compositions (*i.e.* A, B or C) were heated at 1100 °C for 1 h in a vacuum of the order of 8×10^{-5} bar and then either furnace or air cooled to room temperature, or quenched in liquid argon. 1100 °C was selected since this was the optimum solution treatment temperature for both the alloys A and B. The quenching was achieved by rapidly transferring the magnets from a previously well-evacuated furnace tube which was filled with purified argon to a downpipe surrounded by liquid nitrogen. The quenched magnets were then annealed at 600 or 680 °C (magnet A) and 600 °C (magnets B and C) for different times up to 5 h.

The alloy samples were magnetized using a pulse magnetizer and their magnetic properties were measured using a permeameter. The microstructures of the magnets were investigated with an optical microscope and a JEOL 840 A scanning electron microscope and microanalyser.

3. Results and discussion

In Table 1 the permanent magnetic properties of magnet type A in the as-received state are compared with those of such magnets heated at 1100

TABLE 1

Permanent magnetic properties of magnet A in as-received condition, and after being furnace cooled, air cooled and quenched from 1100 °C

	H_{ci} (kA m^{-1})	B_r (mT)	$(BH)_{max}$ (kJ m^{-3})	Squareness factor (%)
As-received	1095.79±4.22	1129.05±1.44	242.07±0.39	0.83
Furnace-cooled from 1100 °C	862.00±5.83	1130.56±4.54	217.02±2.41	0.71
Air-cooled from 1100 °C	786.50±5.45	1128.67±1.70	216.97±4.44	0.75
Quenched from 1100 °C	494.71±1.10	1029.65±1.70	119.48±1.58	0.15

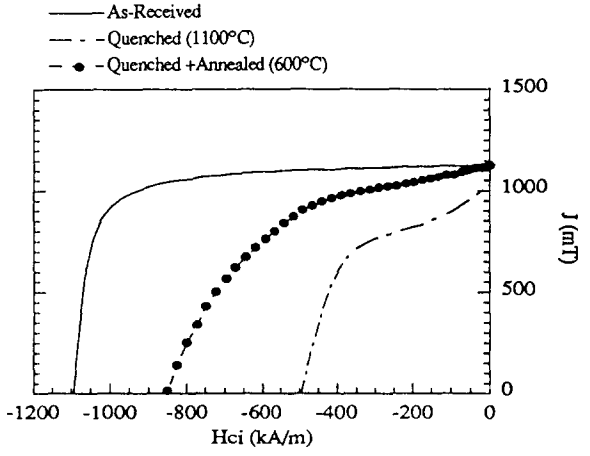


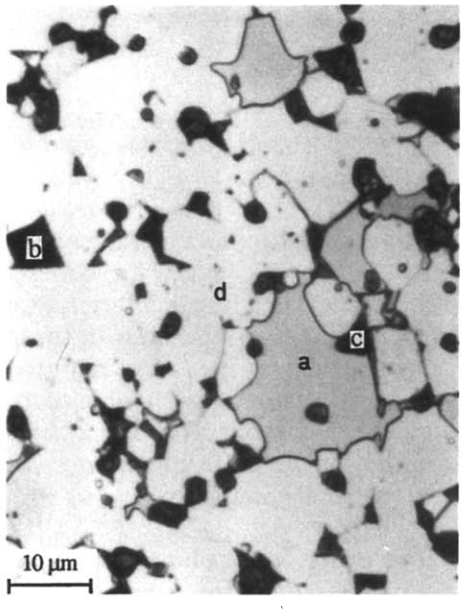
Fig. 1. Demagnetization curves for magnet A in as-received state, and after being quenched, and quenched and then annealed.

°C for 1 h and furnace or air cooled to room temperature (RT) or quenched in liquid argon. There was an increasing fall in H_{ci} with increasing cooling rate, and there occurred a sharp fall in H_{ci} and a very large deterioration in demagnetization loop shape in the quenched magnet compared with those in the as-received magnet. This behaviour on quenching has been reported previously for this type of magnet [1–5] and it has been attributed to intergranular quenching cracks, local strains at grain boundaries and at two-phase interfaces [1], changes in the constitution of the grain boundaries [4] and progressively decreasing wettability of the intergranular phase(s) with increasing cooling rates [5].

In Fig. 1 the demagnetization curves for magnet A are shown in the as-received condition, after quenching (from 1100 °C) and after quenching and annealing (600 °C for 1 h). There was a great deterioration in the shape of the demagnetization loop for this magnet on quenching and the quenched magnet only partially recovered its magnetic properties during annealing at 600 °C for 1 h.

The microstructures of an as-received and a quenched (1100 °C) magnet A (Figs. 2 and 3), determined by electron probe microanalysis (EPMA), were found to consist of (a) $Nd_{1+\epsilon}Fe_4B_4$ and (b) a neodymium-rich eutectic which, together with (c) the oxide, were distributed within (d) an $Nd_2Fe_{14}B_1$ matrix. There was considerable grain growth within the matrix and the 1:4:4 type non-magnetic phase in the magnet heated at 1100 °C and quenched (Fig. 3), thus causing some deterioration in the permanent magnetic properties of magnet A as shown in Table 1 and Fig. 1. The 1:4:4 type non-magnetic phase produces a demagnetizing stray field which can facilitate the nucleation of reversed domains and its growth would cause the magnetic properties to deteriorate further [12].

Table 2 lists the permanent magnetic properties of magnet B in the as-sintered state (sintered at 1060 °C for 1 h followed by furnace cooling to RT), and when furnace cooled, air cooled or quenched after heating at 1100 °C for 1 h. The slight increase in remanence B_r on heating at 1100 °C, in comparison with that of the as-sintered magnet, has been related to some grain growth and improved alignment of the grains at this temperature [13]. There was no significant fall in H_{ci} in the as-sintered magnet on cooling from 1100 °C and the effect of the cooling rate on the resultant H_{ci} values seems to be insignificant. These characteristics are very different from those observed in magnet A and may be attributed to two possibilities: (a) an improved wetting ability of the intergranular phase(s) present in this magnet



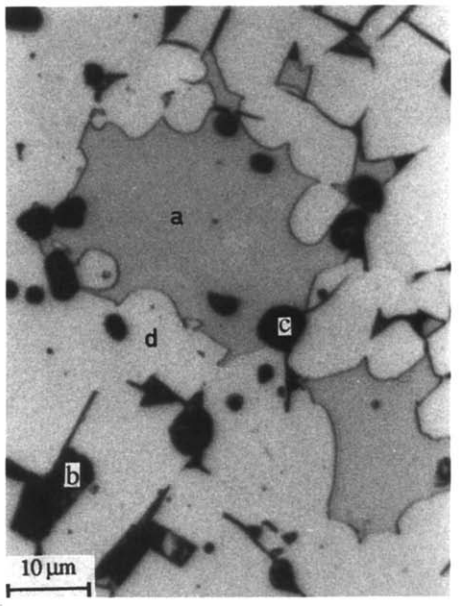


Fig. 2. Microstructure of magnet A in as-received condition: (a) 1:4:4 type phase; (b) neodymium-rich eutectic; (c) oxide and (d) 2:14:1 matrix phase.

Fig. 3. Microstructure of magnet A in quenched (1100 °C) condition: (a) 1:4:4 type phase; (b) neodymium-rich eutectic; (c) oxide and (d) 2:14:1 matrix phase.

TABLE 2

Permanent magnetic properties of magnet B in as-sintered condition, and after being furnace cooled, air cooled and quenched from 1100 °C

	H_{ci} (kA m^{-1})	B_r (mT)	$(BH)_{max}$ (kJ m^{-3})	Squareness factor (%)
As-sintered	678.20±6.57	1068.50±6.82	182.40±3.20	0.47
Furnace-cooled from 1100 °C	631.57±7.40	1158.55±4.82	203.63±4.52	0.45
Air-cooled from 1100 °C	634.20±6.67	1154.42±6.87	201.20±6.20	0.46
Quenched from 1100 °C	628.83±5.03	1160.20±6.44	200.64±4.37	0.43

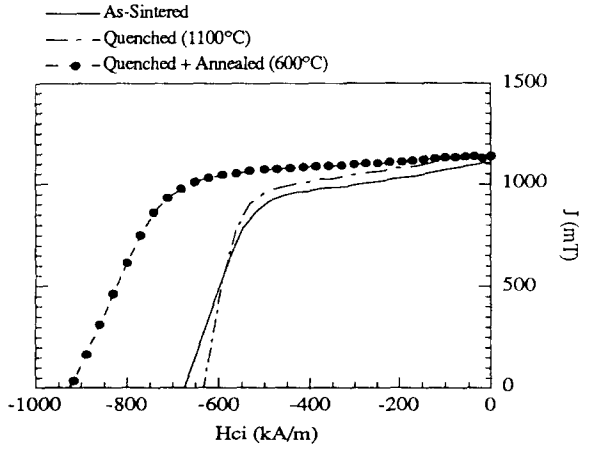


Fig. 4. Demagnetization curves for magnet B in as-sintered state, and after being quenched, and quenched and then annealed.

as a result of the addition of copper and/or (b) a change in the character of the intergranular phases such that the ferromagnetic phases A_1 and A′ are suppressed. The sinterability within this magnet was found to be very good at a sintering temperature of around 1060 °C, and sintered magnets with a density of around 7.45 g cm^{-3} could be produced consistently.

Figure 4 illustrates the second quadrant demagnetization curves for magnet B in the as-sintered state, and after being quenched (1100 °C), and quenched and annealed (600 °C for 1 h). The permanent magnetic properties of the magnet which had been quenched and annealed are given in Table 3. The remarkable improvement in H_{ci} and in the demagnetization loop shape in the quenched and annealed magnet, compared with these properties in one which was as-sintered or only quenched, has been attributed [11] to solute redistribution caused by partial dissolution of an $Nd(Fe_{0.92}Cu_{0.08})_2$ type intergranular phase within the matrix while the magnet was being heated at 1100 °C, and subsequent more uniform formation of this phase during annealing at 600 °C [11, 13]. This annealing treatment has also been shown

TABLE 3

Permanent magnetic properties of magnet B after being quenched from 1100 °C and annealed at 600 °C for 1 h

H_{ci} (kA m^{-1})	B_r (mT)	$(BH)_{max}$ (kJ m^{-3})	Squareness factor (%)
945.40±6.65	1150±5.98	234±4.32	0.78

TABLE 4

Permanent magnetic properties of magnet C in as-sintered condition, and after being furnace cooled, air cooled and quenched from 1100 °C

	H_{ci} (kA m^{-1})	B_r (mT)	$(BH)_{max}$ (kJ m^{-3})	Squareness factor (%)
As-sintered	244.60±9.73	977.80±8.55	58.30±8.08	0.22
Furnace-cooled from 1100 °C	276.42±6.89	1054.40±5.89	106.18±3.63	0.22
Air-cooled from 1100 °C	297.20±4.96	1045.14±8.21	111.94±6.39	0.24
Quenched from 1100 °C	389.00±6.41	1050.20±7.47	135.81±7.41	0.25

to develop a substructure which has the effect of reducing the effective grain size. Details of the microstructural investigations on this magnet have been given elsewhere [11, 14].

The permanent magnetic properties of an as-sintered magnet C are compared in Table 4 with those of magnets C heated at 1100 °C for 1 h and furnace or air cooled to RT or quenched in liquid argon. Although the overall H_{ci} values in magnet C are low, there is a significant improvement in H_{ci} in the as-sintered magnet during heating at 1100 °C and the rate of cooling is crucial in improving the coercivity; *i.e.* increased cooling rates resulted in enhanced H_{ci} values. In previous work [11] it was shown that heating magnet C at 1100 °C and subsequently quenching it in liquid argon resulted in the dissolution of soft magnetic phase(s) such as Nd_2Fe_{17} within the matrix and hence increased H_{ci} values. Thus the fall in H_{ci} caused by reducing the cooling rate (see Table 4) can be attributed to partial re-formation of soft magnetic phase(s) during slow cooling from 1100 °C.

The second quadrant demagnetization curves for magnet C in the as-sintered state (sintered at 1060 °C for 1 h and furnace cooled to RT), and after being quenched (1100 °C), and quenched and annealed (600 °C for 1 h) are compared with one another in Fig. 5. Considerable deterioration in H_{ci} and in the demagnetization loop shape occurred in this magnet on annealing at 600 °C compared with these properties in the quenched magnet, and this has been related to the re-formation of soft magnetic phase(s) during this treatment [11]. This is in contrast with the annealing behaviour of magnets A and B.

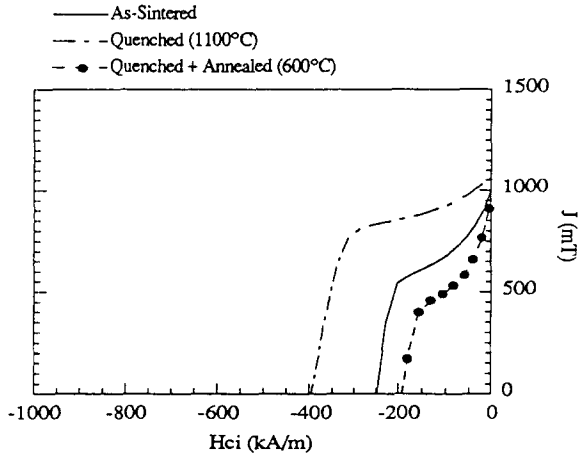


Fig. 5. Demagnetization curves for magnet C in as-sintered state, and after being quenched, and quenched and then annealed.

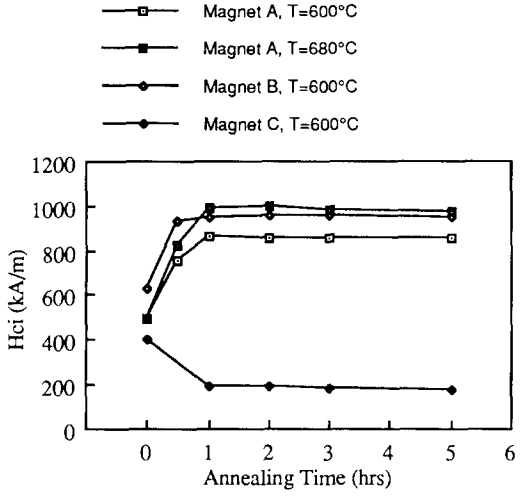


Fig. 6. Variation in H_{ci} values for quenched magnets with annealing time.

The variation in the values of H_{ci} in the quenched magnets A, B and C with annealing time at 600 or 680 °C is shown in Fig. 6. The intrinsic coercivity of magnet A was increased by increasing the annealing time to 1 h but further annealing up to 5 h did not result in any further improvement. Similar behaviour was observed at 680 °C but the overall improvement in H_{ci} was found to be higher than at 600 °C. This indicates that annealing at 680 °C (above the melting point of the intergranular eutectic) is more effective in restoring the coercivity and this can be attributed to a number of factors such as improved wetting of the grains, the elimination and/or reduction of quenching cracks, the elimination and/or reduction of interface strain and the removal of grain boundary steps. In magnet B, a sharp rise in H_{ci} was

observed after annealing for 1 h but further annealing at this temperature did not result in any further improvement in the coercivity. Other work has shown that annealing at higher temperatures results in a smaller improvement in H_{ci} and this has been related to the formation of an optimum $Nd(Fe, Cu)_2$ network at 600 °C. The H_{ci} value for magnet C dropped considerably after annealing at 600 °C for 1 h but further annealing at this temperature did not cause any further decrease. This can be attributed to the formation of some soft magnetic phase or phases and the establishment of a constant amount or a critical distribution after 1 h at 600 °C.

4. Conclusions

The sharp deterioration in the permanent magnetic properties of magnet A on quenching from 1100 °C is related mainly to changes within the intergranular region. Therefore it could be that the wetting character of the intergranular phases in this magnet is damaged by rapid cooling to below the melting point of these phases, so that the permanent magnetic properties of this magnet deteriorate. Alternatively or additionally, the formation of ferromagnetic phases such as A_1 and A′ [8–10] on quenching could also account for the deterioration in the coercivity and loop shape for this magnet.

The coercivity behaviour of magnet B on cooling from 1100 °C at different cooling rates could indicate that copper modifies the wetting character of the intergranular phase(s) so that rapid cooling to below the melting point of the intergranular phases does not affect the wetting character of these phases. Thus copper may modify the sinterability of magnet A. However, the existence of a low melting point intergranular eutectic (485 ± 7 °C) and the absence of the 1:4:4 type phase in the microstructure of this magnet [11] may also have an effect on these properties. Copper may also reduce or eliminate the possible presence of reported ferromagnetic phases such as A_1 and A′ in the grain boundaries and, if so, the H_{ci} values of this magnet would be largely independent of the cooling rate from 1100 °C.

The considerable increase in H_{ci} for magnet C on quenching from 1100 °C can be attributed mainly to the dissolution of the soft magnetic phase(s) within the matrix while the magnet was being heated at 1100 °C. Therefore the dissolution of the soft magnetic phase(s) within the matrix seems to have a greater effect than the possible reduction in coercivity caused by the reduced wetting character of the intergranular eutectic after quenching from 1100 °C [5].

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