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Nd–Fe–B-based magnets: magnetic properties and microstructural appearance with copper addition*

K. G. Knoch, A. Kianvash† and I. R. Harris
School of Metallurgy and Materials, University of Birmingham, Birmingham B15 2TT (UK)

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Abstract

The microstructure of sintered permanent magnets with a composition 17Nd–76.5Fe–5B–1.5Cu was investigated by optical microscopy, electron probe microanalysis and transmission electron microscopy. Using the hydrogen decrepitation processing route, maximum magnetic properties of $H_{cJ}=950$ kA m^{-1} and $(BH)_{max}=230$ kJ m^{-3} were obtained after high temperature homogenization and low temperature annealing. The main effect of the heat treatment procedure was to change the proportion of phases in the four phase microstructure. In addition to Φ and a neodymium-rich phase, two new phases were found: an Nd_1Cu_1-type phase and a phase $Nd_{30}Fe_{65}Cu_5$. The latter seems to play an important role in obtaining high coercivity.

1. Introduction

Regarding the production of rare earth–Fe–B magnets, copper additions were first reported by Shimoda *et al.* [1] in Pr–Fe–B magnets to obtain high coercivity in cast material. Copper-containing Pr–Fe–B alloys are nowadays used for magnet production routes such as die upsetting of melt-spun material followed by diffusion alloying [2] and hot rolling [3] (the latter has also been employed for neodymium-based alloys [4]), which produces anisotropic magnets from powder or cast material. Coercivities above 1000 kA m^{-1} are achieved using compositions of 13.6Pr–80.6Fe–5.3B–0.5Cu, 15Pr–78.5Fe–5B–1.5Cu and 14Nd–79.8Fe–5.2B–1Cu. Thus copper has proved to be a very promising addition even though its effect has not yet been clarified. Allibert [5] reported that copper addition in Nd–Fe–B sintered magnets deteriorated the magnetic properties drastically for amounts of 2 at.% or more for a basic composition 15.15Nd–(79-x)Fe–5.85B–xCu ($0\leq x\leq 4$). Lin *et al.* [6] observed a drastic deterioration of coercivity in 15Nd–77.5Fe–6B–1.5Cu sintered alloys caused by the occurrence of free iron. Contrary to these observations we were able to produce good quality

*Dedicated to Professors W. Bronger and Ch. J. Raub on the occasions of their 60th birthdays.
†Permanent address: Faculty of Engineering, University of Tabriz, Tabriz, Iran.

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Nd–Fe–B–Cu sintered magnets by applying the hydrogen decrepitation (HD) route and a particular two-step heat treatment.

2. Processing

Magnets were produced from cast ingot of the composition 17Nd–76.5Fe–5B–1.5Cu supplied by Rare Earth Products Ltd. (UK). The as-cast alloy was hydrogen decrepitated at room temperature at a H_2 pressure of about 2×10^5 Pa and subsequently roller milled under cyclohexane. The green compacts were sintered at 1060 °C for 1 h in vacuum and furnace cooled to room temperature. After homogenizing the as-sintered magnet at 1100 °C for 1 h, it was quenched in liquid argon. Finally it was annealed at 600 °C for up to 10 h.

3. Magnetic properties

Kianvash and Harris [7] showed that, using the above route, good magnetic properties are obtained. Figure 1 shows the H_{cJ} dependence on the annealing time at 600 °C for an as-sintered and a homogenized magnet. An increase in coercivity of more than 20% is evident in the latter case.

4. Microstructure

The microstructure was studied using optical microscopy, electron probe microanalysis (EPMA) and transmission electron microscopy (TEM).

Figure 2 shows an optical micrograph of an annealed magnet which is not significantly different from that of the as-sintered material. It shows Φ ($Nd_2Fe_{14}B$) as the major phase (bright), an intergranular phase (slightly

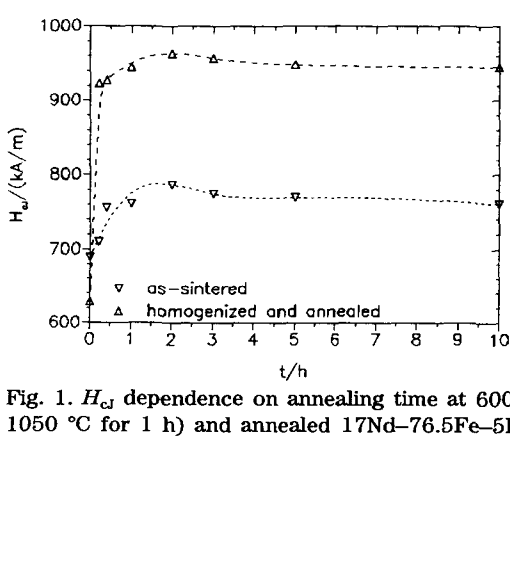


Fig. 1. H_{cJ} dependence on annealing time at 600 °C for as-sintered and for homogenized (at 1050 °C for 1 h) and annealed 17Nd–76.5Fe–5B–1.5Cu magnets.

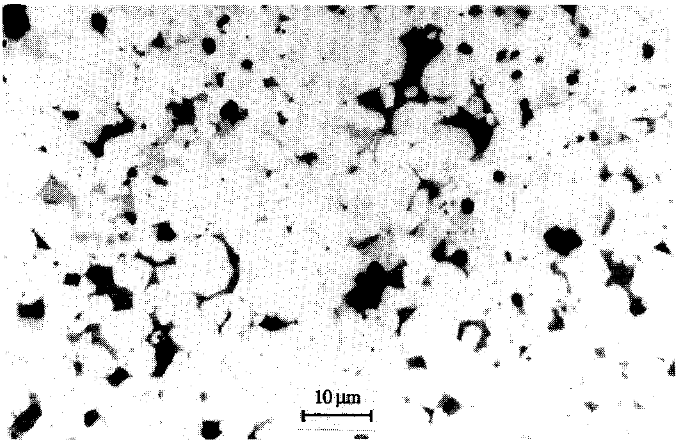


Fig. 2. Optical micrograph of a 17Nd–76.5Fe–5B–1.5Cu magnet in the as-sintered condition showing Φ (white), $Nd_{30}Fe_{65}Cu_5$ (light grey), neodymium-rich areas (dark grey) and oxide (black).

darker), intergranular neodymium-rich eutectic (dark grey) (not resolved on the micrograph) that seems to be composed of neodymium-rich material and another phase. The black roundish areas are oxides. Kianvash and Harris [7] report the existence of two copper-containing grain boundary phases whereas no copper was found in Φ. In addition the Nd_2Fe_{17} phase was found in very isolated areas of as-sintered magnets and a more uniform grain size could be observed in the annealed condition.

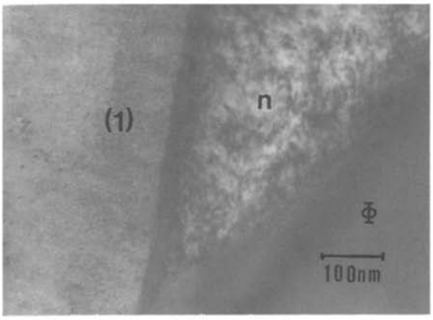
To obtain information about the fine microstructure in the intergranular regions, TEM was applied on as-sintered as well as homogenized and annealed samples. The main findings of these studies are as follows.

(1) No Nd_2Fe_{17} could be detected. This might be because of its very limited occurrence as reported by Kianvash and Harris [7].

(2) Φ proved to be copper free within the detection limit of TEM–energy-dispersive X-ray analysis (about 0.5 at.% Cu).

(3) A small amount of copper was found in the neodymium-rich phase where an average composition of 96.0Nd–3.0Fe–1.0Cu was measured. As known from other magnet compositions, this phase is heavily faulted [8] as can be seen in Fig. 3. This image shows phase boundaries between Φ and neodymium-rich phase and between neodymium-rich and a copper-rich phase.

(4) The copper-rich phase appears to be part of a binary eutectic composed of the neodymium-rich and this copper-rich phase, shown clearly in Fig. 4 where both adopt an alternate lamellar structure. The copper-rich composition exhibits quite a variation from area to area but seems to be based on an Nd_1Cu_1 compound containing a minor amount of iron. It could act as a separator of Φ grains which seemed to be the case in the annealed magnets in particular. However, a statistical analysis is impossible owing to the restricted observation area in TEM.



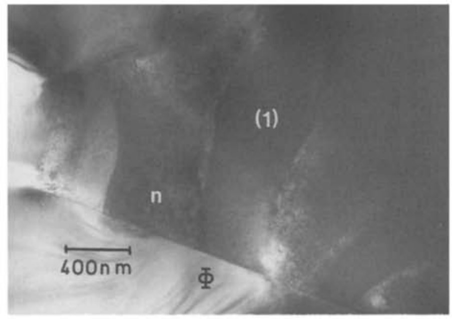


Fig. 3. Eutectic structure of alternating neodymium-rich (n) and copper-rich (1) phase between *Φ* grains.

Fig. 4. Grain boundary region between *Φ*, neodymium-rich phase (n, heavily faulted) and copper-rich phase (1).

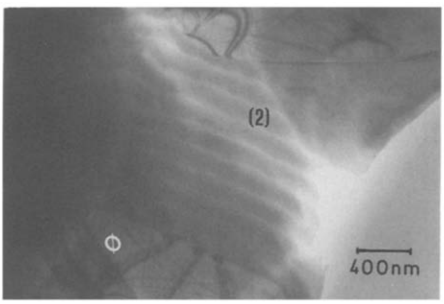


Fig. 5. $Nd_{30}Fe_{65}Cu_5$ phase (2) between *Φ* grains showing its typical appearance in the non-oxidized condition.

(5) Finally the last of the four phases detected can occur as grains as well as a more intergranular type of phase and has a composition $Nd_{30}Fe_{65}Cu_5$. It proved to have a fixed composition within an accuracy of much less than 1 at.%.

This phase has not been reported before but seems to be crucial in obtaining sintered magnets with good magnetic properties from this type of alloy. Thus it occurs much more abundantly in the homogenized and annealed magnet than in the as-sintered case and the annealing results in an increase in coercivity of about 50% (see Fig. 1). A TEM micrograph containing this phase is shown in Fig. 5. The significance of the banded microstructure of this phase is not understood at this stage and this could be a preparation artefact or could be a characteristic of this particular phase. Unfortunately, this phase is prone to oxidation in TEM samples, thus complicating its study.

As mentioned earlier the present results are different from those of Allibert [5] and Fidler [9]. One explanation may be the different composition of 15.15Nd–(79-x)Fe–5.85B–xCu ($0 \leq x \leq 4$) employed by these researchers. On the contrary, an indication of similar results is given in ref. 3 where hotrolled magnets based on the composition 15Pr–76.5Fe–5B–1.5Cu have been investigated. These workers found no copper in $Pr_2Fe_{14}B$ and two different spectra of praseodymium-rich phases which might be related to the new phases detected in our measurements. Recent work [10] in this laboratory on Pr–Fe–B–Cu alloys also indicates the presence of phases similar to those obtained in the present work.

5. Conclusions

The formation of a previously unreported $Nd_{30}Fe_{65}Cu_5$ phase seems to be crucial for the development of coercivity in sintered Nd–Fe–B–Cu-based magnets even though we cannot yet give an explanation for this phenomenon. Whether it is an Nd_1Fe_2-type Laves phase stabilized by copper is not yet clear. Further information about the formation and properties of this phase in particular as well as the copper-rich eutectic phase are necessary and experiments in this regard are already in progress. The results will be published elsewhere [11].

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