THE EFFECTS OF COPPER ON THE MICROSTRUCTURE OF SINTERED Nd-Fe-B TYPE MAGNETS(1)

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It is a well known fact that coercivity may be increased by dopants. The main reason for this is the formation of new phases. In the present work, the effects of Cu on the microstructure of sintered magnets have been investigated using transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX). The $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ permanent magnets were prepared using the hydrogen decrepitation (HD) process. Thermomagnetic analysis showed that there was a ferromagnetic phase apart from the hard magnetic matrix phase in the sintered material. EDX microanalyses showed that this phase has a composition of ~95at% Fe, ~4.5at% Nd and ~0.5at% Cu, which is close to Nd_2Fe_{17} phase. Two types of Cu containing phases were found in the intergranular regions besides the conventional Nd-rich phase.

INTRODUCTION

It has been shown that magnets based on the compositions $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ and $Pr_{16.9}Fe_{79.1}B_4$ produced using the hydrogen decrepitation (HD) process achieve high coercivity after a post sintering heat treatment[1,2]. Annealing the magnets at 1000ºC , resulted in a substantial increase in the intrinsic coercivity for both alloys. In the present work a similar investigation using the HD process has been carried out for magnets based on the alloy $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$. The microstructures of HD sintered permanent magnets have been investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermomagnetic analyses (TMA) have also been employed in the present investigations.

Key words: Permanent magnets, magnetic materials, rare earth, Nd-Fe-B magnets.

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EXPERIMENTAL

The details of the preparation of the HD sintered magnets, post sintering heat treatment and magnetic measurements have all been described in previous papers[1,2]. The annealing treatment was first employed by Shimoda et al.[3] in cast and hot pressed magnets based on the composition $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$. The microstructural microanalyses were carried out using a JEOL 840A scanning electron microscope (+EDX) and a JEOL 4000FX transmission electron microscope (+EDX). In order to prepare the TEM specimens, thin slices were cut from the magnets and the discs for TEM were then mechanically ground, dimpled to a thickness of approximately 80 µm and finally thinned by argon ion beam milling at 5 - 6 keV. Thermomagnetic analyses were carried out in a Sucksmith balance.

RESULTS AND DISCUSSION

Figure 1 shows the variation of magnetic properties with milling time for slow cooled HD magnets of the $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy, both as-sintered and annealed at 1000°C for 24 hours. As can be seen a small increase in the magnetic properties occurs with this post sintering heat treatment for this alloy, but no iHc peak, as in the case of the PrFeB(Cu) alloys[1,2],

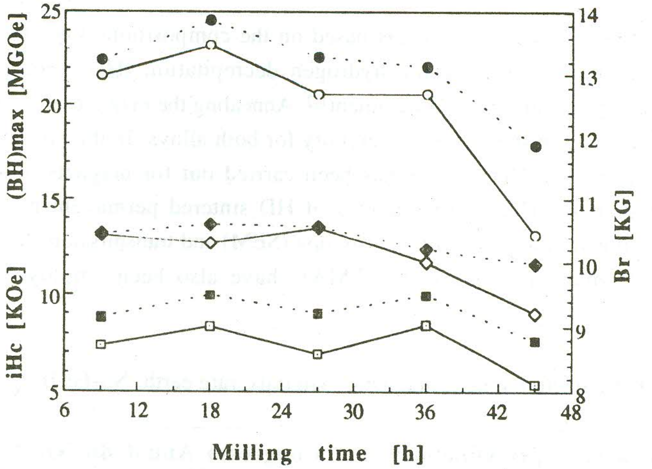


Fig.1. Variation of (BH)max (o) and iHc (▣) and Br (◊) with the milling time for slow cooled HD magnets of $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy (Black/dashed : annealed 1000°C, 24 hours).

has been found. Similar results have also been obtained in $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ magnets produced using shorter annealing time[4].

Figure 2 shows a TEM micrograph of a matrix grain. Occasionally some particles could be seen in the matrix grains. EDX microanalyses showed that the particles have a composition of ~ 95at% Fe, ~4.5at% Nd and ~0.5at% Cu, which is close to Nd_2Fe_{17} phase. The Fe-rich particles are detrimental to the hard magnetic properties . It has been reported that there is a dissolution of the soft ferromagnetic phase (Nd_2Fe_{17}) within the matrix phase during the high temperature annealing[4] and this increases the coercivity. Similar behaviour has been observed with Pr_2Fe_{17} phase in Pr-Fe-B-Cu permanent magnets[5]. The chemical conpositions of the phases detected by EDX on the scanning electron microscope in the sintered $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ magnet are listed in Table 1.

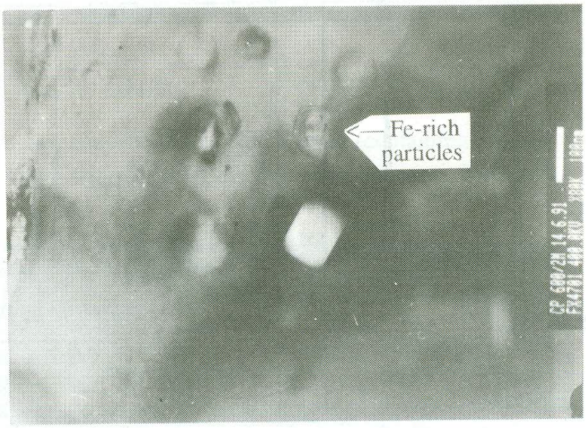
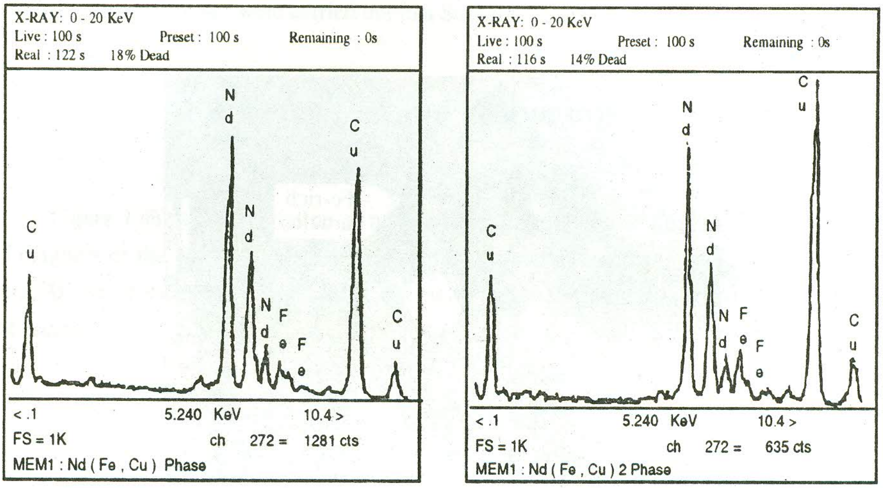


Fig. 2. TEM micrograph showing some Fe-rich particles in the matrix grains.

Table 1. Chemical compositions (at%) of the phases detected in the sintered $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ magnets. (Error bar : ±0.5at%)

Phases	Nd (at%)	Fe (at%)	Cu (at%)
Matrix	13	86	<1
Nd-rich	93	6	<1
NdCu	45.9	5.4	48.7
$NdCu_2$	36.2	7.9	55.9
Fe-rich	4.5	94.8	<1

It can be seen that less than 1at% Cu substitutes for Fe in the $Nd_2Fe_{14}B$. Therefore, Cu cannot induce a significant modification of the intrinsic properties of this phase (T_c, M_s or H_a). Cu mainly enters the Nd-rich liquid and forms new intergranular phases. Two types of Cu containing phases were found in the intergranular regions besides the conventional Nd-rich phase. Figure 3 shows their X-ray spectra. The ratio in at% of Nd/Cu was determined to be close to 1 for phase (a) and close to 0.5 for phase (b).



(a) NdCu (containing~5at% Fe) **(b) NdCu2 (containing~8at% Fe)**

Fig. 3. X-ray spectra of NdCu and NdCu2 in the sintered $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ magnet.

Figure 4 clearly shows that the NdCu grain (containing ~5at%Fe) is separated in the intergranular region from the fcc + complex bcc Nd-rich phase. Figure 5 shows a $NdCu_2$ (containing ~8at% Fe) phase with 36at% Nd, 8at% Fe and 56at% Cu in the Nd-rich region. The contrast between NdCu and the conventional Nd-rich region was not clear. Two intergranular phases NdCu and $NdCu_2$ were also observed by Fidler[6] in Cu-substituted Nd-Fe-B sintered magnets and the crystal structures of these two phases were suggested to be orthorhombic. A $Nd_{30}Fe_{65}Cu_5$ phase has also been found in Nd-Fe-B-Cu magnets[7] and a $Pr_{34}Fe_{62}Cu_4$ phase in the Pr-Fe-B-Cu permanent magnets[5].

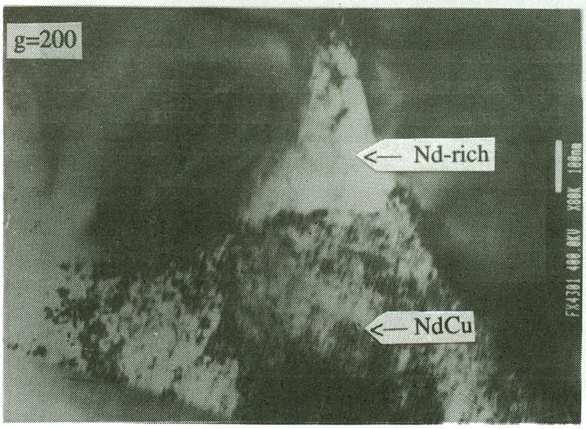


Fig. 4. TEM micrograph showing a NdCu phase (containing ~5at%Fe) within the triple point region. Diffracting vectors marked, electron beam direction, B, near [001].

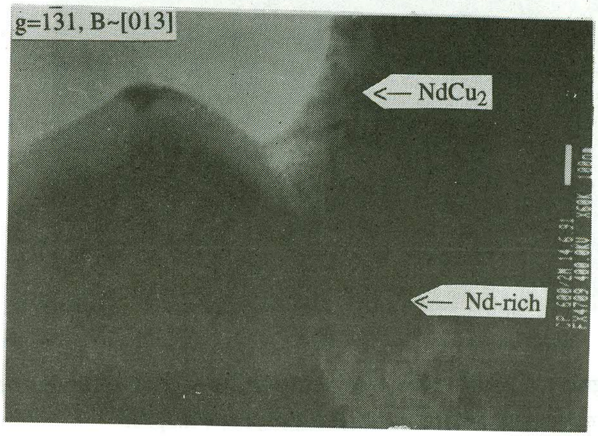


Fig. 5. TEM micrograph showing the NdCu$_2$ (containing ~8at%Fe) in the intergranular Nd-rich region.

From these observations, it can be concluded that the majority of Cu is used to form new intergranular NdCu (containing ~5at%Fe) and NdCu$_2$ (containing ~8at%Fe) phases. This changes the volume fraction of the grain boundary surrounding the $Nd_2Fe_{14}B$ grains. Figure 6 shows a typical TEM micrograph of a $Nd_2Fe_{14}B$ - $Nd_2Fe_{14}B$ grain boundary and figure 7 shows a triple point region. The images show the very good wettability between the matrix grains in the sintered material.

Fig.6. TEM micrograph of a matrix grain boundary in the sintered $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ magnet.

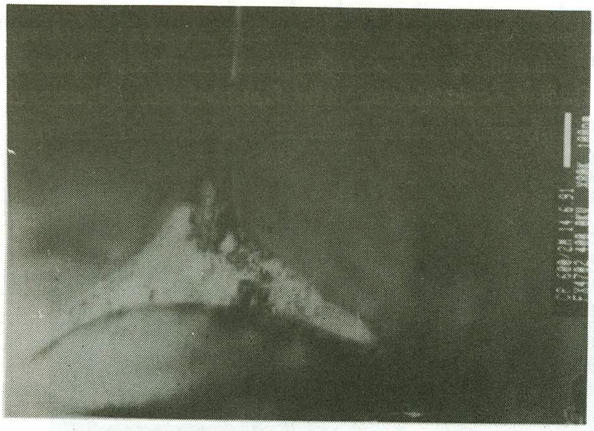


Fig. 7. TEM micrograph of a triple point region showing very good wettability between the Nd-rich phase and the matrix in the sintered $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ magnet.

A thermomagnetic analysis curve of the as-sintered magnet is presented in fig.8. The small magnetization variation (increasing between the temperatures 150 to 200 °C) can be ascribed to the competing effects of increasing temperature on the degree of saturation of the sample (due to decreasing anisotropy of the misaligned sample) and the value of the saturation magnetization. The TMA showed that, in addition to the matrix phase (Tc=313°C), there was a lower Curie point ferromagnetic phase with a Tc around 86°C, and this can be attributed to the presence of a 2:17 type phase in these magnets. This phase (Nd_2Fe_{17}) has a reported Curie point as low as 54°C[8] and as high as 84 °C [9].

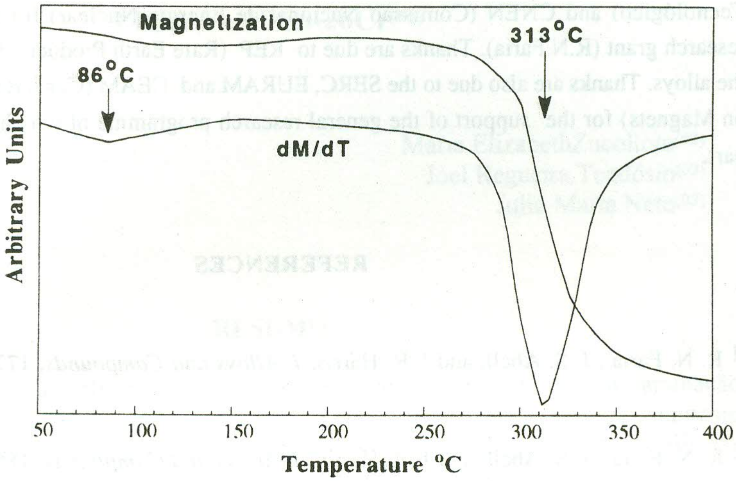


Fig. 8. Magnetization (non-saturated) versus temperature for the $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ HD magnet in the as-sintered condition (error±5°C).

CONCLUSIONS

The intrinsic coercivity of $Nd_{17}Fe_{76.5}B_5Cu_{1.5}$ HD permanent magnets cannot be increased substantially by annealing. Two types of Cu containing phases were found in the intergranular regions besides the conventional Nd-rich phase: NdCu and $NdCu_2$. Occasionally some particles could be found in the matrix grains and EDX microanalyses showed that these particles have a composition of ~ 95at% Fe, ~4.5at% Nd and ~0.5at% Cu, which is close to Nd_2Fe_{17} phase. TMA showed that this ferromagnetic phase has a Curie temperature around 86°C. TEM images showed the very good wettability between the matrix grains in the sintered material.

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