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Authors

Koestler, C.
Ramesh, R.
Echer, C.J.

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MICROSTRUCTURE OF MELT SPUN Nd-Fe-Co-B MAGNETS

C. Koestler, R. Ramesh, C. J. Echer and G. Thomas

Department of Materials Science and Mineral Engineering, University of California, and
National Center of Electron Microscopy, Lawrence Berkeley Laboratory, 1 Cyclotron
Road, Berkeley, California 94720

Abstract

In this paper we report results on microstructural characterization of melt spun $\text{Nd}_{17}\text{Fe}_{77}\text{B}_6$ and $\text{Nd}_{15}(\text{Fe}_{1-x}\text{Co}_x)_{77}\text{B}_8$ ribbons using high resolution electron microscopy, x-ray microanalysis and microdiffraction. In general, the microstructure consists of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and one or more grain boundary phases. In all these materials no $\text{Nd}_{11}\text{Fe}_4\text{B}_4$ phase was observed. The grain boundary phase in the Co-free samples appear mainly at multi-grain junctions and is a Nd-rich, crystalline (fcc) phase, whereas the Co-containing specimens comprise two different fcc grain boundary phases. The structural and microchemical data indicate that these are likely to be ferromagnetic and that they contain significantly less Nd than the grain boundary phase of the Co-free samples. The average matrix grain diameter is about 80 nm, but there are always some areas in every specimen where the grain diameter is very small (about 20 nm) or very large (more than 300 nm) causing differences in the size of the grain boundary phases both at the triple grain junctions and between the grains.

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I. INTRODUCTION

It is well known /1-5/ that the substitution of cobalt for iron raises the Curie temperature T_C of the hard magnetic $Nd_2Fe_{14}B$ phase and enhances the thermostability in the temperature range which is important for technical applications. However, in powder metallurgical produced Nd-Fe-B magnets Co decreases the coercivity possibly because of the occurrence of magnetic minority phases which act as nucleation sites for reverse domains /6/. In rapidly quenched Nd-Fe-B ribbons magnetization reversal is supposed to be controlled by pinning of domain walls at Nd-rich precipitates /7,8/. Minority phases are, therefore, essential in these melt spun materials to enhance the pinning of domain walls.

Fuerst and Herbst /9/ have shown that for melt spun alloys having the $Nd_{13.5}[(Fe_{1-x}Co_x)_{95}B_5]_{86.5}$ starting composition the intrinsic coercivity iH_c and the remanence J_r decrease with increasing Co-concentration; for example, the coercivity decreases from 12.5 kOe ($x=0$) to 9.5 kOe ($x=0.5$). Their x-ray diffraction analyses indicate that for $x<0.5$ the ribbons consist principally of $Nd_2(Fe_{0.5}Co_{0.5})_{14}B$. For $x=0.5$ some contamination by secondary phases, in particular $NdCo_2$, is observable and only in the $x=0.75$ and $x=1.0$ samples it was possible to identify the major component as Nd_2Fe_{17} -type with $Nd_2(FeCo)_{14}B$ also present.

In contrast to this data are the results of melt spun ribbons with a nominal composition of $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ prepared by Wecker and Schultz /10,11/. As can be seen in Fig.1(a) not only does the Curie temperature increase with increasing Co-content but also the intrinsic coercivity increases to a maximum value of 24 kOe for $x=0.3$ Co (Fig.1(b)). Even at $x=0.5$ iH_c does not drop below the value of 20 kOe of the Co-free sample. The variation of J_r with Co concentration qualitatively reflects the change of the saturation magnetization J_s with the incorporation of Co into the $Nd_2Fe_{14}B$ phase /2/. The x-ray diffraction patterns of the Co alloyed ribbons clearly showed an additional peak which could be attributed to a $Nd(FeCo)_2$ Laves phase /12/.

Microchemical analysis of these $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ samples performed by Hütten and Haasen /13-15/ using a field ion microscope (FIM) in combination with an atom probe (AP) time of flight mass spectrometer indicated that there was only one grain boundary phase detectable which was described as $Nd_{23}(Fe_{1-x}Co_x)_{75}B_2$.

Thus the objective of the present study was to determine the number, composition and structure of the grain boundary phases in melt spun $\text{Nd}_{17}\text{Fe}_{77}\text{B}_6$ and $\text{Nd}_{15}(\text{Fe}_{1-x}\text{Co}_x)_{77}\text{B}_8$ permanent magnets in the magnetic optimum state using analytical and high resolution transmission electron microscopy (TEM).

II. EXPERIMENT

The isotropic $\text{Nd}_{17}\text{Fe}_{77}\text{B}_6$ and $\text{Nd}_{15}(\text{Fe}_{1-x}\text{Co}_x)_{77}\text{B}_8$ specimens were prepared as ribbons with a thickness of 30-35 μm and a length of 15-30 mm at Siemens AG, Erlangen, FRG. The preparation of the ribbons, the experimental procedures employed to obtain the optimum magnetic state and the x-ray diffraction and magnetic measurements are described in detail by Wecker and Schultz /8,10,11/.

The ribbons were mounted on a copper-grid and electron transparent thin samples were made by argon ion-milling, using a liquid nitrogen specimen holder and carried out at 6 kV with a gun current of 0.4 mA. The milling was completed in about 3-4 hours.

The samples were examined using a Philips 400 TEM operating at 100 kV and a JEOL 200CX TEM operating at 200 kV. To avoid any specimen contamination the samples were cooled down to liquid nitrogen temperature. Both microscopes are fitted with regular Be window energy dispersive x-ray (EDX) detectors. The latter is also fitted with an ultrathin window EDX detector that enables the detection of elements with atomic number greater than or equal to six and with an electron energy loss spectroscopy (EELS) detector. Spectral deconvolution and quantification were carried out on a KEVEX 8000 system software using theoretically generated thin foil k-factors. By acquiring a minimum of 10^5 counts statistical significance of the data was ensured. Also for these elements (Fe, Co, Nd) absorption corrections are negligible.

For high resolution imaging another JEOL 200CX electron microscope at 200 kV was used. This microscope is fitted with a high resolution top entry stage and has a demonstrated point-to-point resolution of 2.3 $\text{\AA}$.

III. RESULTS AND DISCUSSION

A. The Nd₁₇Fe₇₇B₆ sample

Magnetic measurements by Wecker and Schultz /8/ indicated that optimally quenched Nd₁₇Fe₇₇B₆ and Nd₁₅Fe₇₇B₈ specimens possess higher values for coercivity (20.0 kOe and 22.2 kOe) and remanence (6.4 kG and 7.1 kG) than samples with the stoichiometric composition Nd_{11.8}Fe_{82.3}B_{5.9} ($\mu H_c=4.4$ kOe). Therefore Nd₁₇Fe₇₇B₆ samples were used for this study.

TEM investigations of the Nd₁₇Fe₇₇B₆ ribbons yielded a two phase microstructure as observed by Mishra /7,17/ for melt spun Nd_{13.5}Fe_{81.0}B_{5.5}. The microstructure of the Nd₁₇Fe₇₇B₆ specimens consists of randomly oriented Nd₂Fe₁₄B matrix grains which are polyhedral in shape and of a Nd-rich, crystalline grain boundary phase appearing mainly at multi-grain junctions. The diameter of the grain boundary phase is 100-800 Å and it does not surround all matrix grains as reported by Mishra /7,16/. In his samples the grain boundary phase is amorphous and not crystalline. Contrary to the observations by Hadjipanayis and Kim /17/ on ribbons with off-stoichiometric composition and to the results of Hütten und Hassen /13,18/ on melt spun Nd_{15.3}Fe_{74.6}B_{10.1} no Nd_{1.1}Fe₄B₄ phase was found in this Nd₁₇Fe₇₇B₆ alloy.

Fig.2 which shows the typical microstructure for a Nd₁₅(Fe_{0.7}Co_{0.3})₇₇B₈ specimen is also a typical image for the microstructure of the Co-free samples. The average matrix grain diameter is about 80 nm but there are always some areas where the grain diameter is less than 20 nm or more than 300 nm associated with differences in the size of the grain boundary phase. With increasing Nd₂Fe₁₄B grain size the extent of the grain boundary phase increases in all dimensions. When it is large in extent the grain boundary phase is polycrystalline and in areas where the matrix grains are smaller (and hence the grain boundary phase are smaller) the grain boundary phase is single crystal. These areas with smaller and larger matrix grains comprise about 20-30 % of the volume and include areas where the matrix grains have a platelet shape as can be seen in Fig.3. Obviously the difference in the grain size depends on differential cooling, reported also by Wecker and Schultz /8/. They found that sometimes at the upper ribbon surface which experienced lower quenching rates the Nd₂Fe₁₄B grains are larger (400-500 nm). A more uniform average grain size with a value of 30 nm was observed by Mishra /16/. Hadjipanayis and Kim /17/ found for melt spun Nd₁₅Fe₇₇B₈ that the matrix grains are coarser (≈ 1500 Å) than in ribbons with the stoichiometric composition (≈ 800 Å).

EDX-spectra of the matrix and the grain boundary phases together with microdiffraction patterns of the grain boundary phase are shown in Figs.4(a-c). To obtain single crystal microdiffraction and statistically significant microanalytical information a 200 Å probe size was used. Quantification led to the expected values for the Nd₂Fe₁₄B phase and to a composition of around 75 at% Nd and 25 at% Fe for the grain boundary phase confirming previous measurements by Hütten and Haasen /13/ with FIM/AP on melt spun Nd_{15.3}Fe_{74.6}B_{10.1} ribbons. Furthermore, all microdiffraction patterns could be indexed as fcc with a lattice parameter $a_0=5.6$ Å indicating that the grain boundary phase in the Co-free melt spun material has the same composition and structure as was found for the grain boundary phase in sintered RE-Fe-B by Ramesh et al. /19,20/. Using Auger spectroscopy and a ultrathin window EDX detector Ramesh et al. also found that the presence of oxygen stabilized the fcc phase. However a fcc phase is not observed in this composition range in the Nd-Fe binary phase diagram although the Nd-Fe system exhibits a eutectic decomposition around 640°C /21/ with a Nd to Fe ratio of 72 to 28, similar to the 75 to 25 composition of the grain boundary phase. On the Nd₁₇Fe₇₇B₆ ribbons, a thin oxygen surface layer was detectable using a ultrathin window EDX detector although no significant difference in the oxygen content between the matrix and the grain boundary phase was seen. On the other hand FIM/AP measurements /13-15,18/ with a lateral resolution of about 2 nm and an atomic depth resolution of melt spun Nd_{15.3}Fe_{74.6}B_{10.1} never showed any evidence of oxygen in the grain boundary phase. Thus it appears that there is less or no oxygen in the grain boundary phase of the melt spun samples compared to the sintered material. Due to the small size of the grain boundary phase the presence of boron was not detectable with a parallel EELS detector. However the B content is less than 1 or 2 at% /7,13/ and thus is below the detection limit of the technique.

Figs.5(a) is a high resolution micrograph of a small grain boundary phase in a Co-free ribbon. The enlarged image in Fig.5(b) shows clearly the lattice fringes in the grain boundary area, again confirming the fcc and therefore crystalline structure of the triple junction regions. Care was of course taken to ensure that the appropriate imaging conditions were met so as not to confuse interpretation of such fringe images.

These TEM results confirmed what Wecker and Schultz /8/ expected for the optimally quenched off-stoichiometric Nd₁₇Fe₇₇B₆ ribbons. Because of the higher overall Nd content the volume fraction of the grain boundary phase is higher (>10 %) than in the ribbons with the stoichiometric composition Nd_{11.8}Fe_{82.3}B_{5.9}; for example, the amorphous grain boundary phase in the optimally quenched Nd_{13.5}Fe_{81.0}B_{5.5} specimens

comprises only 5 % of the volume [7]. Furthermore Mishra [7,16] has shown for these samples that the domain walls are mainly pinned in the second phase at the grain boundaries. This result seems to be valid for all melt spun material [17]. Therefore if the amount of the grain boundary phase is higher the characteristic magnetic values iH_c , J_r and the energy product $(BH)_{max}$ should be larger. That is the case for the $Nd_{17}Fe_{77}B_6$ ribbons investigated in this study (Fig.1(b)).

B. The $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ samples

The cobalt substituted samples exhibited microstructural features that were different from those of the cobalt-free samples. Figs.6(a-c) show bright field TEM images of the $x=0.3$ Co sample. It must be emphasised that the overall microstructural features of all the cobalt-containing specimens are similar and hence the experimental results for the $x=0.3$ Co sample will be discussed in detail here. The images in Figs.6(a-c) illustrate the large range of grain sizes observed in these samples. Fig.6(a) depicts the region with an average grain size of 40 nm; (b) shows a region with an average grain size of 100 nm and (c) is an image from a region of average grain size of >300 nm. As in the case of the cobalt free samples, a grain boundary phase is observed in all three regions (indicated by arrows). The structure and composition of the grain boundary phase(s) was determined by microdiffraction and x-ray microanalysis.

Microdiffraction analyses were carried out for all three samples and two different types of grain boundary phases were observed. Fig.7(a-c) show representative microdiffraction patterns of a $x=0.3$ Co sample from the [001], [011] and the [233] zone axis orientations of a fcc structure. The fcc structure is clearly determined from the symmetry of the [011] zone axis microdiffraction pattern. Analysis of these microdiffraction patterns yielded a lattice parameter of 5.4 Å. Fig.7(d-f) show microdiffraction patterns from the other grain boundary phase that is observed in all three Co substituted samples. Analysis of these patterns, as in the case of Figs.7(a-c), showed an fcc structure and yielded a lattice parameter of 7.3 Å. These microdiffraction patterns were all obtained from different regions of the samples. In order to determine the cause for the difference in the lattice parameters, these grain boundary regions were analysed by EDXS and EELS. Figs.8(a-c) show typical EDX spectra from the matrix phase, the 5.4 Å fcc grain boundary phase and from the 7.3 Å fcc grain boundary phase respectively, from

the $x=0.3$ Co sample. The quantified data from the three spectra are also included in the inserts to each spectrum. In Tables I, II and III the microanalytical data for the matrix $\text{Nd}_2(\text{Fe}_{1-x}\text{Co}_x)_{14}\text{B}$ phase, the $5.4 \text{ \AA}$ grain boundary phase and the $7.3 \text{ \AA}$ grain boundary phase are respectively summarized. EELS analysis did not indicate the presence of either oxygen nor boron in both these phases, within the detectability limit of the technique. Examination of the composition of the two grain boundary phases indicates that the $7.3 \text{ \AA}$ fcc phase has a composition close to $\text{Nd}(\text{FeCo})_2$. The lattice parameter of this phase agrees well with that published in the literature for NdCo_2 /22/ and NdFe_2 /22/. Since it is known that both these phases are ferromagnetic, it is reasonable to expect that the $\text{Nd}(\text{FeCo})_2$ fcc grain boundary phase is also ferromagnetic. Wecker and Schultz /11/ examined melt spun magnets of cobalt rich compositions and found a dip in the magnetization M vs temperature T plot at about 400°C . They also found that a rapidly quenched $\text{Nd}_2(\text{Fe}_{0.5}\text{Co}_{0.5})_8$ sample contains at least three magnetic phases with Curie temperatures of about 180°C , 360°C and 650°C . It is likely that the presence of the $\text{Nd}(\text{FeCo})_2$ phase will affect the magnetic properties of the magnet. The observation of this phase is consistent with the x-ray diffraction data of Wecker and Schultz /11/, who observed the $\text{Nd}(\text{FeCo})_2$ phase for $x \geq 0.3$ Co. In our experiments, this phase is observed for all three cobalt contents. It is however possible that this phase is not detectable by x-ray diffraction for $x \leq 0.3$, since the extent of this phase increases with the overall cobalt content of the alloy thus highlighting the advantage of TEM over x-ray techniques for detecting small volume fractions of any phase. An interesting observation from Table III is that the Co content of this phase is always higher than that expected from the nominal composition of the alloy. In other words, cobalt preferentially partitions into this phase. This also suggests that the volume fraction of this phase should increase with increase in the Cobalt content of the alloy, as is observed experimentally.

EDX microanalysis results of the fcc grain boundary phase $\text{Nd}_{20}(\text{Fe}_{1-x}\text{Co}_x)_{80}$ with a lattice parameter of $5.4 \text{ \AA}$ are summarized in Table II. The cobalt content of this phase, unlike the $\text{Nd}(\text{FeCo})_2$ phase, follows the nominal alloy composition. Thus it is likely that the volume fraction of this phase is relatively unchanged with increase in the Cobalt content of the alloy. Examination of the existing literature does not reveal the presence of a phase with such a composition and lattice parameter, although the phase $\text{Nd}_6\text{Fe}_{23}$ (about 20 at% Nd) is known to exist in the fcc structure with a lattice parameter of $12.1 \text{ \AA}$ /23,24/. It is likely that this phase is a metastable phase formed due to the rapid cooling conditions prevailing during solidification of the melt. Hütten and Haasen /15,16/, through FIM/AP experiments, have shown that a minority phase of composition

$\text{Nd}_{23}(\text{Fe}_{1-x}\text{Co}_x)_{75}\text{B}_2$ exists in similar melt spun alloys. This composition is closest to that obtained for the 5.4 Å fcc grain boundary phase in this study. The small amount of boron (2 at%), is below the detectability limit of EELS and hence was not resolved. The large Fe to Co content in this phase suggests that this phase should also exhibit magnetic order. Hence it is also likely to affect the properties of the magnet.

The extent and distribution of the grain boundary phases changed with the size of the matrix grains. In regions where the matrix grains were small (about 20-30 nm), this phase was observed as single crystalline regions at the multi-grain junctions, as illustrated in the high resolution image in Fig.9(a). In this case the regions of dark contrast are the 5.4 Å fcc grain boundary phase. Fig.9(b) shows a similar example of the 7.3 Å grain boundary phase. The partial penetration of this phase into the two grain boundaries of the matrix phase is to be noted. In several regions, the grain boundary phase, especially the 7.3 Å phase was observed to be heavily faulted or microtwinning, as shown in the example in Fig.9(c). When the size of the matrix grains is large (greater than 300 nm), the grain boundary phase becomes polycrystalline and both grain boundary phases are observed. The $\text{Nd}(\text{FeCo})_2$ phase is observed to a larger extent in such areas as illustrated by the bright field image and inserted microdiffraction patterns in Fig.10.

If the matrix grain is completely surrounded by the relatively soft magnetic fcc grain boundary phase (it should possess low magnetocrystalline anisotropy), it is likely that the matrix grains are isolated from one another. When the cobalt content is increased to $x=0.5$, this type of microstructure is frequently observed, as illustrated in the high resolution lattice fringe image in Fig.11. In this micrograph, the matrix grains denoted by "M" are almost completely surrounded by the fcc grain boundary phases denoted by "GB". The formation of such a microstructure will influence the magnetic properties. For example the large difference in crystalline anisotropy that can exist between the matrix phase and the cubic grain boundary phases, can lead to significant pinning of domain walls at these grain boundary phases.

One significant difference of the microstructural observations in this work and that of Mishra [7,16] is the amorphous phase observed at almost all the grain boundaries by Mishra. In this study an amorphous phase was only infrequently observed. Fig.12 shows a high resolution image of one grain boundary which does show the presence of an amorphous phase in a $\text{Nd}_{15}(\text{Fe}_{0.9}\text{Co}_{0.1})_{77}\text{B}_8$ sample. Invariably, the grain boundaries were free of such a phase, while at the grain junctions the fcc phases were observed.

Microstructure Property Correlations

Hirosawa et al. /25/ have reported single crystal measurements of the anisotropy field of $\text{Nd}_2(\text{Fe}_{1-x}\text{Co}_x)_{14}\text{B}$. They showed that at room temperature, the anisotropy field is not significantly different for values of $x \leq 0.38$ Co. However for higher values of x , the anisotropy field decreases. From Table I it can be seen that the composition of the 2-14-1 phase follows the alloy composition. Thus for the $x=0.5$ sample, the anisotropy field of the matrix phase is likely to be significant lower than for the specimens with lower Co content. This seems to be one of the causes for the drop in the iH_C at $x \geq 0.4$ Co as seen in Fig.1. The increase in iH_C for values $x \leq 0.3$ Co can be attributed to the increasing volume fractions of the grain boundary phases, which can act as potent pinning sites. Thus the maximum in iH_C is due to the balance between the above two effects. The decrease in remanence J_r with x after a very shallow maximum at $x \approx 0.2$ is also due to the increasing volume fractions of the two grain boundary phases. So also, the increasing Co content of the matrix phase leads to a decrease in the saturation magnetization, as was shown by Hirosawa et al. /2/.

IV. CONCLUSIONS

The microstructure of optimally quenched Nd-Fe-B magnets with and without Co additions has been investigated using microdiffraction, analytical electron microscopy and high resolution electron microscopy. In samples without Co, the overall microstructure is similar to that observed by other workers, although in contrast to Mishra very few grain boundaries are laced with an amorphous phase. The grain boundary phase is crystalline and has an fcc structure with a nominal composition of $\text{Nd}_{75}\text{Fe}_{25}$, in general agreement with earlier work. In the case of the Co-substituted samples, two other fcc phases have been observed. One of them has a lattice parameter of $7.3 \text{ \AA}$ with a composition of $\text{Nd}(\text{FeCo})_2$, while the other has a lattice parameter of $5.4 \text{ \AA}$ and a composition of $\text{Nd}_{20}(\text{Fe}_{1-x}\text{Co}_x)_{80}$. This $5.4 \text{ \AA}$ fcc phase is a new phase in this alloy system, heretofore unobserved, although the composition is close to that of $\text{Nd}_6\text{Fe}_{23}$ (fcc, $a=12.1 \text{ \AA}$). The Co content of the $7.3 \text{ \AA}$ fcc phase is significantly higher than that of the alloy, suggesting that Co stabilizes the $7.3 \text{ \AA}$ fcc phase by preferentially partitioning into it. The volume fraction of these two fcc phases increases with increasing Co content of the alloy, and for $x=0.5$, some of the matrix grains are surrounded by the grain boundary phases. In all the

cases, the $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ phase was never observed. The increase in the iH_c of the magnet up to $x=0.3$ Co as shown in Fig.1(b) can be explained by the increase in the fraction of the grain boundary phases leading to better pinning of the domain walls. In this composition range from $x=0$ to $x=0.3$ Co, the effective anisotropy field of the matrix phase does not change appreciably [25]. For higher values of x , the iH_c drops since the anisotropy field of the matrix phase drops significantly for Co contents greater than 0.4 as was shown by Hirosawa et al. [25].

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TABLE I Composition of the $\text{Nd}_2(\text{Fe}_{1-x}\text{Co}_x)_{14}\text{B}$ matrix phase for the $x=0.1, 0.3$ and 0.5 Co-containing melt spun $\text{Nd}_{15}(\text{Fe}_{1-x}\text{Co}_x)_{77}\text{B}_8$ ribbons.

Co content x	Nd [at%]	Fe [at%]	Co [at%]
0.1	14.7 ± 0.6	76.9 ± 0.4	8.4 ± 0.5
0.3	13.9 ± 1.4	59.3 ± 1.0	26.8 ± 1.9
0.5	14.3 ± 0.4	43.4 ± 0.4	42.3 ± 0.5

Note: Boron is not detected by the Be window x-ray detector. The composition is normalized with respect to the amounts of Nd, Fe and Co.

TABLE II Composition and lattice parameter of the $\text{Nd}_{20}(\text{Fe}_{1-x}\text{Co}_x)_{80}$ fcc grain boundary phase for the $x=0.1, 0.3$ and 0.5 Co-containing melt spun $\text{Nd}_{15}(\text{Fe}_{1-x}\text{Co}_x)_{77}\text{B}_8$ ribbons.

Co content x	Nd [at%]	Fe [at%]	Co [at%]
0.1	19.8 ± 0.6	72.6 ± 0.2	7.6 ± 0.4
0.3	19.5 ± 1.3	54.0 ± 2.6	26.5 ± 2.6
0.5	20.9 ± 1.8	43.1 ± 1.4	36.0 ± 2.7

$$a_0 = (5.4 \pm 0.2) \text{ \AA}$$

Note: Boron is not detected by the Be window x-ray detector. The composition is normalized with respect to the amounts of Nd, Fe and Co.

TABLE III Composition and lattice parameter of the Nd(FeCo)₂ fcc grain boundary phase for the three Co substituted melt spun Nd₁₅(Fe_{1-x}Co_x)₇₇B₈ ribbons.

Co content x	Nd [at%]	Fe [at%]	Co [at%]
0.1	30.8 ± 1.9	60.2 ± 2.6	9.0 ± 0.9
0.3	31.7 ± 3.8	34.2 ± 3.7	34.1 ± 2.5
0.5	28.1 ± 2.2	26.0 ± 3.1	45.9 ± 2.3

$$a_0 = (7.3 \pm 0.2) \text{ \AA}$$

Note: Boron is not detected by the Be window x-ray detector. The composition is normalized with respects to the amount of Nd, Fe and Co.

FIGURE CAPTIONS

- Fig.1 a. Curie temperature as a function of Co content x in optimally quenched $\text{Nd}_{15}(\text{Fe}_{1-x}\text{Co}_x)\text{77B8}$
b. Coercivity iH_c and remanence J_r of optimally quenched ribbons vs Co content x .
- Fig.2 Bright field TEM micrograph of a $\text{Nd}_{15}(\text{Fe}_{1-x}\text{Co}_x)\text{77B8}$ sample showing randomly oriented matrix grains and the grain boundary phase (some marked by arrows).
- Fig.3 Bright field image of platelet matrix grains and of the grain boundary phase (marked by arrows) in a $\text{Nd}_{17}\text{Fe77B6}$ sample.
- Fig.4 EDX spectra of the matrix (a), the grain boundary phase (b) and microdiffraction patterns of the grain boundary phase (c) in the $\text{Nd}_{17}\text{Fe77B6}$ sample.
- Fig5. (a-b) High resolution TEM micrographs of a small grain boundary phase in a $\text{Nd}_{17}\text{Fe77B6}$ sample.
- Fig.6 Bright field images of areas with 40 nm (a), 100 nm (b) and more than 300 nm (c) average matrix grain size in a $\text{Nd}_{15}(\text{Fe}_{0.7}\text{Co}_{0.3})\text{77B8}$ sample.
- Fig.7 Microdiffraction patterns and lattice parameters of the $\text{Nd}_{20}(\text{Fe}_{0.7}\text{Co}_{0.3})_{80}$ fcc grain boundary phase (a-c) and of the $\text{Nd}(\text{FeCo})_2$ fcc grain boundary phase (d-f).
- Fig.8 EDX spectra of the $\text{Nd}_{20}(\text{Fe}_{0.7}\text{Co}_{0.3})_{14}\text{B}$ matrix phase (a), the $\text{Nd}_{20}(\text{Fe}_{0.7}\text{Co}_{0.3})_{80}$ fcc grain boundary phase (b) and of the $\text{Nd}(\text{FeCo})_2$ fcc grain boundary phase (c). Boron is not detectable by a Be window EDX detector. The B content was although under the detectability limit of a parallel EELS detector. The small Cl peak in Fig8(c) is due to etching the constituents with HCl prior to melting.
- Fig.9 High resolution images of the 5.4 Å $\text{Nd}_{20}(\text{Fe}_{0.5}\text{Co}_{0.5})_{80}$ grain boundary phase in the region of dark contrast (GB) (a), the 7.3 Å $\text{Nd}(\text{FeCo})_2$ grain boundary phase

(marked by arrows in b) and of a faulted 7.3 Å grain boundary phase (marked by arrows in c) of a $\text{Nd}_{15}(\text{Fe}_{0.5}\text{Co}_{0.5})_{77}\text{B}_8$ sample.

Fig.10 Bright field TEM micrograph showing the polycrystalline grain boundary phases of a $\text{Nd}_{15}(\text{Fe}_{0.5}\text{Co}_{0.5})_{77}\text{B}_8$ sample. A and B are the diffraction patterns of the 5.4 Å and the 7.3 Å grain boundary phases, respectively.

Fig.11 High resolution image illustrating the almost complete surrounding of the matrix (M) by the grain boundary phase (GB) in a $\text{Nd}_{15}(\text{Fe}_{0.5}\text{Co}_{0.5})_{77}\text{B}_8$ sample.

Fig.12 High resolution image of a small amorphous grain boundary phase between two matrix grains in a $\text{Nd}_{15}(\text{Fe}_{0.9}\text{Co}_{0.1})_{77}\text{B}_8$ sample.

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a.

b.

Fig. 1

XBL 889-3196

Fig. 2

XBB 880-9823

BF

XBB 880-9824

Fig. 3

Fig. 4

XBB 880-9826

Fig. 5

XBB 880-9825

Fig. 6 XBB 880-9692

Fig. 7

XBB 880-9562

XBL 8810-3573

Fig.8

XBB 888-8226

Fig. 9a

Fig. 9b

XBB 888-7740

Fig. 9c

XBB 880-9821

Fig. 10

XBB 880-9822

Fig. 11

XBB 888-8227

Fig. 12

XBB 888-7736

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720