Abstract—By appropriate annealing of rapidly quenched Nd\textsubscript{2}Fe\textsubscript{13.1}B (2.05<\delta<147.6) the amount and microstructure of the Nd\textsubscript{2}Fe\textsubscript{14}B grains in the Nd-rich matrix were systematically controlled and correlated with coercivity, $\mu_0 H_c$. For optimally annealed Nd\textsubscript{2}Fe\textsubscript{13.1}B an increase in Nd concentration enhances $\mu_0 H_c$ of the Nd\textsubscript{2}Fe\textsubscript{14}B grains (from 1.2 T in Nd\textsubscript{2.05}Fe\textsubscript{13.1}B to 2.75 T in Nd\textsubscript{14.7}Fe\textsubscript{13.1}B at 290 K) and promotes the growth of the Nd\textsubscript{2}Fe\textsubscript{14}B grains elongated in shape. The largest observed coercivity, $H_c \sim 2.75$ T is over 80% of the theoretical limit expected for Stoner-Wohlfarth coherent rotation behavior including demagnetization effects.

Introduction

In theory, the nucleation field of randomly-oriented, non-interacting, single domain magnetic particles with $K_1 \gg K_2$ can be calculated as $\mu_0 H_N^{\text{min}} = 0.5(2K_1/M_s^2)N$ if the magnetic moments of these particles coherently rotate in the applied field [1]. Here $K_1$ and $K_2$ are the magnetocrystalline anisotropy constants, $M_s$ is the spontaneous magnetization and $N$ is the demagnetization factor. However, experimentally obtained values of the coercive field are at least two times smaller than the theoretically predicted values. The main reason for this discrepancy is that the coercive field in magnetic materials reflects both intrinsic magnetic properties and the microstructure of the material. Thus, only in materials with optimal microstructure, i.e., with non-interacting single domain magnetic particles, one might expect to approach the theoretical predicted values. Moreover, magnetic particles with a large enough $K_1$ are desired to ensure coherent rotation of their magnetic moments.

Nd-Fe-B represents an ideal system because it is possible to form the high anisotropy Nd\textsubscript{2}Fe\textsubscript{14}B grains in a non-magnetic matrix over a wide range of compositions as shown in the ternary Nd-Fe-B diagram, Bushow et. al. [2] (Fig. 1). The ternary diagram was obtained analyzing melt spun Nd-Fe-B samples thermally annealed below 1173 K (973 K for Nd-rich corner). Previously, systematic work has been done on the rapidly quenched Nd-Fe-B samples with compositions along the tie-line connecting the Nd\textsubscript{2}Fe\textsubscript{14}B and Nd\textsubscript{1.1}Fe\textsubscript{1.1}B\textsubscript{4} phases [3]. Unfortunately, in this compositional region the soft magnetic Fe and Fe-B phases may precipitate during annealing introducing centers for domain wall nucleation that will directly reduce coercivity. For this reason we prepared a series of melt-spun samples along the tie-line connecting Nd\textsubscript{2}Fe\textsubscript{14}B and pure Nd. As shown [4] there is a wide range of compositions around the tie-line where combination between the Nd\textsubscript{2}Fe\textsubscript{14}B phase and Nd-rich paramagnetic phases can be formed by annealing rapidly quenched samples. The motivation was to obtain randomly oriented, single
domain, Nd$_2$Fe$_{14}$B particles embedded in a non-magnetic Nd matrix. By systematically changing the amount of the non-magnetic Nd matrix, the effect of the interaction on coercivity between Nd$_2$Fe$_{14}$B was also investigated.

The change in the composition will have an effect on the microstructure and therefore on the magnetic properties of the Nd-Fe-B samples. Thus, in this paper we will also put an emphasis on the microstructural investigation of Nd-Fe-B using electron microscopy.

**Experimental Techniques**

The Nd$_x$Fe$_{13.1}$B ($2.05 \leq \delta \leq 147.6$) alloys, prepared by arc-melting, were melt-spun in an argon atmosphere using a Cu wheel with a surface speed of 35 m/s. The as-quenched and annealed ribbons were characterized by differential scanning calorimetry (DSC), X-ray and thermomagnetic analysis (TMA) [5,6]. Results show that by changing the Nd concentration the ratio between the Nd$_2$ Fe$_{14}$B and Nd-rich can be systematically controlled in optimally annealed Nd$_x$Fe$_{13.1}$B [5,6]. The magnetic measurements are performed with a SQUID magnetometer at 290 K with a maximum external field, $\mu_0 H_{ext} = 5.5$ T. In order to ensure a random crystallographic orientation of the Nd$_2$Fe$_{14}$B grains in the Nd$_x$Fe$_{13.1}$B ribbons, coercivity was measured in both ribbon and powdered ribbon (with particle sizes below 50 µm) samples. The details of the powder sample preparation and analyses of the SQUID measurements have been previously presented [5]. The M(H) loop of Nd$_x$Fe$_{13.1}$B (except for Nd$_{2.05}$Fe$_{13.1}$B) contains contributions from the ferromagnetic Nd$_2$Fe$_{14}$B and paramagnetic Nd-rich phases. The Nd-rich phase consists of mainly α-Nd and a few percent γ-Nd so it was assumed that α-Nd correctly accounts for the paramagnetic contribution in Nd$_x$Fe$_{13.1}$B. Microstructural analysis of Nd$_x$Fe$_{13.1}$B was carried out by conventional transmission electron microscopy (TEM) and energy-filtered imaging using inner-shell ionization edges in electron energy-loss spectroscopy. The later was done on Nd$_{0.38}$Fe$_{13.1}$B ($\delta = 38.1$, 147.6) by selecting energy windows around the Nd M$_{4,5}$ edge for mapping Nd and energy windows around the Fe L$_{2,3}$ edge for mapping Fe. For each map, one energy window was positioned at the onset of the characteristic edge to obtain the signal due to the energy-loss of the transmitted electrons (post-edge image) and two energy windows before the edge to extrapolate the background below the ionization edge (pre-edge 1 and pre-edge 2 images) [7]. The widths of the energy windows were 20 eV for Fe and 30 eV for Nd. The Nd and Fe jump ratio images, obtained by dividing the post-edge by the pre-edge 2 image [7]. The Nd$_2$Fe$_{14}$B grains are dark in the Nd map and bright in the Fe map.
Results and Discussions

The annealing is crucial to obtain a large coercivity of the rapidly quenched Nd\textsubscript{38.1}Fe\textsubscript{13.1}B samples. Fig. 2 shows the dependence of the coercive field, $\mu_0 H_c$, on the annealing time for Nd\textsubscript{38.1}Fe\textsubscript{13.1}B. The corresponding microstructure of these samples is presented in Fig. 3. The M(H) loop shows that the as-quenched Nd\textsubscript{38.1}Fe\textsubscript{13.1}B exhibits both soft magnetic behavior (Fig. 2a). The selected area diffraction and bright field images, Fig. 3a, show that the as-quenched sample has both amorphous (diffuse ring pattern) and nano-crystalline structure (Fig. 3a). The largest $\mu_0 H_c$ was obtained after annealing for 2

Figure 2. Coercive field $\mu_0 H_c$ as a function of the annealing time for Nd\textsubscript{38.1}Fe\textsubscript{13.1}B annealed at 873 K. M-H loops for a) as quenched, b) annealed for 2 min., and c) annealed six hours, Nd\textsubscript{38.1}Fe\textsubscript{13.1}B ribbons.

Figure 3. The grain size of Nd\textsubscript{2}Fe\textsubscript{14}B as a function of the annealing time in Nd\textsubscript{38.1}Fe\textsubscript{13.1}B annealed at 873 K. Fig. 3a) bright field image of as quenched Nd\textsubscript{38.1}Fe\textsubscript{13.1}B with selected area diffraction pattern, Fig. 3b) and 3c) energy filtered images of Nd\textsubscript{38.1}Fe\textsubscript{13.1}B annealed at 2 and 64 min. respectively and 3d) bright field images of Nd\textsubscript{38.1}Fe\textsubscript{13.1}B annealed at 6 hours with [112] selected area diffraction pattern of Nd\textsubscript{2}Fe\textsubscript{14}B.
min. at 873 K (Fig. 2b). This sample contains plate-like Nd$_2$Fe$_{14}$B grains, 100 nm long, embedded in the Nd-rich matrix. The size of the Nd$_2$Fe$_{14}$B grains is close to the single magnetic domain size (~100 nm) that is the optimal microstructure for obtaining a large $\mu_0 H_c$. Further annealing decreases $\mu_0 H_c$ due to the formation of grains significantly larger than that for single magnetic domains.

For example, for samples annealed for six hours $\mu_0 H_c$ decreases by about 30% (Fig. 2c) and the Nd$_2$Fe$_{14}$B grains are larger than 0.5 μm (Fig. 3d). As shown the microstructure of Nd$_2$Fe$_{13.1}$B is very sensitive to the annealing conditions. Moreover, DSC measurements show that the crystallization temperature of the Nd$_2$Fe$_{14}$B phase decreases with an increase of the Nd concentration for δ ≤ 38.1 in Nd$_{147.6}$Fe$_{13.1}$B. Thus, to obtain the optimal microstructure both annealing time and temperature are adjusted separately for each composition. The optimal annealing conditions for Nd$_{2.05}$Fe$_{13.1}$B, Nd$_{6}$Fe$_{13.1}$B (δ = 3.8, 6, 8.9, 12.7) and Nd$_{147.6}$Fe$_{13.1}$B (δ = 38.1, 147.6) ribbons were found to be 4 min. at 923 K, 2 min. at 873 K and 4 min. at 823 K, respectively.

The M(H) measurements show that the coercivity of the Nd$_2$Fe$_{14}$B phase in Nd$_{2.05}$Fe$_{13.1}$B (Fig. 4) increases with an increase in the Nd concentration from 1.2 ± 0.03 T for Nd$_{2.05}$Fe$_{13.1}$B to 2.75 ± 0.03 T for Nd$_{147.6}$Fe$_{13.1}$B. The error bars were estimated from measuring four different ribbon samples with the same composition. Fig. 4 shows that the discrepancy between the values of coercivity obtained for the ribbon and powder samples is small, confirming the random orientation of the Nd$_2$Fe$_{14}$B grains in the ribbons. The microstructure of Nd$_2$Fe$_{13.1}$B also changes with the Nd concentration. The bright field image (Fig. 4) shows that the Nd$_{2.05}$Fe$_{13.1}$B sample contains uniform distribution of the polyhedral Nd$_2$Fe$_{14}$B grains elongated in shape as can be seen from the bright field image of Nd$_2$Fe$_{13.1}$B and the energy-filtered image of Nd$_{147.6}$Fe$_{13.1}$B (Fig. 4). Detailed analyses of Nd$_{147.6}$Fe$_{13.1}$B [5] confirms that the Nd$_2$Fe$_{14}$B grains are platelets with an average size of $a \times b \times c = 100 \times 40 \times 25$ nm. The high resolution lattice image of a representative Nd$_2$Fe$_{14}$B grain in optimally annealed Nd$_{147.6}$Fe$_{13.1}$B shows that the shortest side of the plate is along the crystallographic c-axis [5].
For such randomly oriented, non-interacting, single domain, magnetic particles, the coercivity calculated from the Stoner-Wohlfarth model [1] should be equal to about half of the nucleation field \( \mu_0 H_c \approx 0.5 \mu_0 H_N \). Since, in Nd\(_2\)Fe\(_{14}\)B at 290 K, \( K_1 > 4K_2 \), the coercivity can be calculated [8] as,

\[
\mu_0 H_c = 0.5 \mu_0 H_N = \frac{(K_1 + K_2)}{M_s} - 0.5(N_{||} - N_{\perp})M_s \quad N_{||} \text{ and } N_{\perp} \text{ are the demagnetization factors parallel and perpendicular to the c-axis of the Nd\(_2\)Fe\(_{14}\)B platelets and can be determined assuming that the Nd\(_2\)Fe\(_{14}\)B grains in Nd\(_{147.6}\)Fe\(_{13.1}\)B are ellipsoids with axes } a = 20 \text{ nm, } b = 50 \text{ nm and } c = 12.5 \text{ nm [9]. } K_1, K_2, \text{ and } M_s \text{ values of Nd\(_2\)Fe\(_{14}\)B are taken from the literature [10]. It follows that the coercivity of the Nd\(_2\)Fe\(_{14}\)B grains in Nd\(_{147.6}\)Fe\(_{13.1}\)B should be equal to } \mu_0 H_c = 3.33 \text{ T. Thus the measured coercivity of the Nd\(_2\)Fe\(_{14}\)B grains in Nd\(_{147.6}\)Fe\(_{13.1}\)B is about 83% of the theoretical value of coercivity obtained from the Stoner-Wohlfarth model for an assembly of randomly oriented, non-interacting, single domain particles.}

**Conclusions**

By appropriate annealing of rapidly quenched Nd\(_{\delta}\)Fe\(_{13.1}\)B (2.05 < \( \delta < 147.6 \)) the amount and microstructure of the Nd\(_2\)Fe\(_{14}\)B grains in the Nd-rich matrix were systematically controlled. For optimally annealed Nd\(_{\delta}\)Fe\(_{13.1}\)B an increase in Nd concentration enhances \( \mu_0 H_c \) of the Nd\(_2\)Fe\(_{14}\)B grains (from 1.2 T in Nd\(_{2.05}\)Fe\(_{13.1}\)B to 2.75 T in Nd\(_{147.6}\)Fe\(_{13.1}\)B at 290 K) and promotes the growth of the Nd\(_2\)Fe\(_{14}\)B grains elongated in shape. The largest observed coercivity, \( H_c \sim 2.75 \text{ T} \) is over 80% of the theoretical limit expected for Stoner-Wohlfarth coherent rotation behavior including demagnetization effects.

**References**