MICROSTRUCTURE AND INTERPHASE MAGNETIC COUPLING IN Nd$_2$Fe$_{14}$B/α-Fe NANOCOMPOSITES OBTAINED BY MECHANICAL MILLING AND SHORT TIME ANNEALING

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The effects of short time annealing and soft phase pre-milling on the structural and magnetic properties of 6 h milled Nd$_2$Fe$_{14}$B/10wt% Fe magnetic nanocomposites were investigated. The X-ray diffraction peaks of Nd$_2$Fe$_{14}$B disappeared after milling due to crystal structure damage, this effect being more pronounced when using pre-milled Fe. After annealing, the characteristic peaks of Nd$_2$Fe$_{14}$B were restored with a limited growth of the α-Fe crystallites. The best exchange coupling was obtained for the samples which contain unmilled Fe as the soft phase. The maximum coercive field is 0.61 T. The samples containing pre-milled Fe have lower coercive field values, but show a higher remanence. The Nd$_2$Fe$_{14}$B/α-Fe exchange coupling is analysed.

Key words: soft/hard magnetic nanocomposites, interphase exchange coupling, ball milling, short time annealing.

1. INTRODUCTION

In recent years permanent magnets have steadily increased in importance, becoming crucial components in many devices and advanced technologies. The demand for permanent magnets is strongly increasing due to their applications in environmental technologies such as wind turbines and electric vehicles. Soft/hard magnetic nanocomposites comprise a fine mixture of exchange coupled hard and soft magnetic phases, ensuring both high coercivity and high remanence [1]. The soft/hard Nd$_2$Fe$_{14}$B/Fe$_3$B and Nd$_2$Fe$_{14}$B/α-Fe nanocomposite systems exhibit interesting properties for fundamental research as well as applications [2–6]. Particularly, in addition to an increase in remanence, the presence of Fe in exchange coupled nanocomposites could lead to increased thermal stability [7, 8].

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higher corrosion resistance [9], however, this could also decrease the coercivity. The microstructure, especially the crystallinity of the hard phase and the crystallite size of the soft magnetic phase, is a critical parameter regarding the strength of the soft/hard interphase exchange coupling [10]. However, the preservation of the hard phase crystal structure, controlling the soft crystallite sizes and obtaining a microstructural homogeneity during the preparation process is difficult to accomplish. So far, a number of techniques have been used to obtain soft/hard nanocomposites [5], such as: melt-spinning [11], mechanical milling [12, 13], hot deformation [14] and thin film deposition [15], followed by various annealing procedures.

The structural and magnetic properties of 6 h and 8 h mechanically milled (MM) Nd$_2$Fe$_{14}$B+10 wt% α-Fe nanocomposites were previously studied [12, 16]. After milling, the samples showed poor crystallinity and a high defect density. The restoration of the hard phase crystal structure without an excessive growth of the soft phase crystallites could be achieved through properly selected annealing parameters. Two types of annealing processes were tested [12]: classical annealing at 550 °C for 1.5 h and short time annealing at 700–800 °C for 0.5–3 minutes. For the 8 h milled samples, both annealing types led to the recrystallization of the hard phase, however, the samples which were annealed for short times at higher temperatures showed smaller Fe crystallites and a better recrystallization of the hard phase which led to higher coercivities and a stronger interphase exchange coupling [12]. For the classically annealed samples, the best exchange coupling was obtained for the 6 h milled samples [12]. Consequently, a better interphase exchange coupling could be expected for samples milled for 6 h followed by short time annealing at higher temperatures. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) investigations on milled SmCo$_5$/α-Fe nanocomposites showed that for short milling times (2–4 h MM), the composite mixture might not be homogeneous [17]. Longer milling times, from 6 to 8 h, homogenize the powder mixture [17, 18]. In this paper we analyze the effect of the short time annealing on the microstructure and interphase exchange coupling of the 6 h milled Nd$_2$Fe$_{14}$B+10 wt% α-Fe nanocomposites.

2. EXPERIMENTAL DETAILS

The Nd$_2$Fe$_{14}$B ingot was prepared by induction melting in a purified Ar atmosphere, followed by annealing in vacuum at 950 °C for 68 h. The ingot was crushed and the resulting powder was sieved through a 500 μm sieve. The starting materials for the soft phases were commercial NC 100.24 Fe powder (Höganäs product) below 40 μm and Fe powder dry milled for 4 h under Ar in a high-energy planetary mill (Fritsch Pulverisette 4). The sieved Nd$_2$Fe$_{14}$B powder was mixed with the Fe powders in a weight ratio of 90% Nd$_2$Fe$_{14}$B/10% Fe. The mixtures
were dry-milled under Ar for 2, 4, 6 and 8 h respectively. The milling vials (with a volume of 80 ml) and balls (Ø 10 mm in diameter) were made of 440 C hardened steel. In both cases, the pre-milling of Fe and the milling of the composite powders, the ratio between the rotation speed of the disc and the relative rotation speed of the vials was $\Omega/\omega = 333/–900$ rpm with a ball-to-powder weight ratio of 10:1. The samples of milled powder were wrapped in tantalum foil, sealed in quartz tubes and annealed in an inert Ar atmosphere using a preheated furnace at 700, 750 and 800 °C for times ranging from 0.5 to 2.5 minutes. After annealing, the sealed samples were quenched in water.

The structure and microstructure of the nanocomposites were investigated using a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation and Bragg-Brentano focusing geometry. The X-ray diffraction measurements were performed on powder samples using the $\theta$–2$\theta$ scan. The average $\alpha$-Fe crystallite sizes were determined from the full width at half maximum (FWHM) of the (211) diffraction peak of $\alpha$-Fe at $2\theta = 82.3^\circ$ using Scherrer’s formula [19]. The FWHM values were obtained by fitting the (211) $\alpha$-Fe peak using a normalized pseudo-Voigt function. For the calculation of the average crystallite size, the instrumental contribution to the peak width was subtracted from the obtained FWHM values. The instrumental broadening was measured from the X-ray diffraction pattern of a reference sample (recrystallized standard elemental Fe powder). Scanning electron microscopy (SEM) and X-ray microanalysis studies were performed on a Jeol-JSM 5600 LV microscope equipped with an energy dispersive X-ray EDX spectrometer (Oxford Instruments Inca 200 software). The mechanical hardness of the Fe powders was measured using an atomic force microscope equipped with a XE 70 TD 21562 Sapphire Cantilever nanoindentor with a diamond tip, the data being interpreted using the Oliver and Pharr model [20]. For magnetic measurements, the powder samples were blocked in epoxy resin. The demagnetization curves were recorded at room temperature using the extraction method in applied fields up to ±10 T [21]. Considering isolated spherical magnetic particles we used a demagnetization factor of 1/3 for the magnetic data and for the calculation of the internal field, $H_{\text{int}}$.

3. RESULTS AND DISCUSSIONS

3.1. INFLUENCE OF SHORT TIME ANNEALING

In order to study the influence of short time annealing on the microstructure and magnetic properties of Nd$_2$Fe$_{14}$B + 10wt% Fe nanocomposites we prepared milled samples of Nd$_2$Fe$_{14}$B powder mixed with non pre-milled Fe powder below 40 µm.
Fig. 1 – XRD patterns for the as-milled (2, 4 and 6 h) and annealed Nd₂Fe₁₄B+10 wt% α-Fe samples. The XRD pattern of the unmilled starting sample is given for comparison.

For the as-milled samples, the XRD peaks corresponding to the hard magnetic phase get wider with milling time and disappear after 6 h of milling due to the damaging of the Nd₂Fe₁₄B crystal structure and increased milling induced strain and defect densities, Figure 1.

Table 1

Average α-Fe crystallite sizes (d), FWHM values of the α-Fe (211) XRD peak, coercive field ($μ_0H_c$) and remanent magnetization values ($M_r$) for the 6 h MM annealed samples.

The values for 8 h MM annealed samples are given for comparison

<table>
<thead>
<tr>
<th>Milling time (h)</th>
<th>Annealing temperature (°C)</th>
<th>FWHM ± 0.1 (°)</th>
<th>Annealing time (min)</th>
<th>$d$ ± 2 (nm)</th>
<th>$μ_0H_c$ ± 0.01 (T)</th>
<th>$M_r$ ± 1 (Am²/kg)</th>
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<tr>
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<td></td>
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<td></td>
<td>0.91</td>
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<tr>
<td>750</td>
<td>1.57</td>
<td>0.5</td>
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<td>0.07</td>
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<tr>
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</table>
During annealing, in addition to the recovery of the hard magnetic phase crystal structure, the α-Fe phase is also influenced. The FWHM values of the α-Fe (211) XRD peak at 2θ = 82.3° decrease with increasing annealing temperature and/or time – Table 1. The release of milling-induced stress for α-Fe occurs at temperatures around 200 °C, the samples annealed at high temperatures (700–800 °C) even for short times being considered stress-free [12]. Thus, after annealing at high temperatures the XRD peak broadening can be correlated only to the crystallite sizes of soft phase which increase with annealing temperature and/or time – Figure 2.

![Graph showing annealing time dependence of the average crystallite sizes of α-Fe](image)

Fig. 2 – Annealing time dependence of the average crystallite sizes of α-Fe as derived from the X-ray diffraction for the 6h MM annealed samples. The crystallite sizes of the 8h MM annealed samples are shown for comparison.

The average soft crystallite sizes of the 6 h MM annealed samples are larger than those of the 8 h MM ones, however, after annealing these values remain in the 5–20 nm range meaning that the excessive growth of the soft phase crystallites was hampered during the short time annealing. The average soft crystallite sizes of the 6 h MM short time annealed samples are smaller than those of the samples obtained when the classic annealing method is used – Table 1. The results of the SEM-EDX investigations on annealed 6h MM Nd₂Fe₁₄B+10wt% Fe samples are shown in Figure 3. The powder particles are formed of agglomerations of nanocrystallites, Fig. 3a. Also, the annealed samples are very homogeneous; the distributions of Nd and Fe being identical, Figure 3(b,c).
Fig. 3 – SEM image (a) and EDX analysis of the same area for Nd (b) and Fe (c) for the 6h MM Nd$_2$Fe$_{14}$B+10 wt% α-Fe sample, annealed at 750 °C for 2 min.

Fig. 4 – Demagnetization curves (a) and dM/dH versus H curves (b) for the annealed Nd$_2$Fe$_{14}$B+10 wt% Fe samples, measured at room temperature.
The demagnetization curves, after magnetization at 10 T, of the samples annealed at 700 °C suggest that the hard and soft magnetic phases are badly coupled, Figure 4(a). The hysteresis curves of the samples annealed at 750 and 800 °C mainly show a single magnetic phase behaviour. The room temperature $dM/dH$ vs. $H$ plots of the annealed samples show two peaks, one at low field values of ~0.2 T and the other centred around 0.5–0.7 T, Figure 4(b). The $dM/dH$ peak at low fields could correspond to weakly coupled or uncoupled Fe and Nd$_2$Fe$_{14}$B crystallites, while the peak at higher fields could be attributed to the exchange coupled nanocomposite.

The heat treatment at 700, 750 and 800 °C for times up to 2.5 minutes ensure the restoration of the hard magnetic phase and nanometre dimensions for the crystallites of the two phases, which result in a better interphase exchange coupling. For the 6 h MM annealed samples at 700 °C, the $dM/dH$ vs. $H$ curves show an intense peak at low magnetic fields, confirming the weak coupling between the hard and soft phases. With increasing temperature and/or time, the exchange coupling strength increases progressively as result of restoration of the Nd$_2$Fe$_{14}$B crystal structure during annealing. If the α-Fe crystallites become larger, then the exchange coupling will be weakened, as evidenced by the evolution of $dM/dH$ curves. The coercivity increases with both annealing temperature and time up to 0.61 T for the sample annealed at 750 °C for 2 minutes, Table 1. This behaviour can be correlated with the gradual restoration of the crystal structure of Nd$_2$Fe$_{14}$B during the annealing processes. Because of the effect of annealing on the crystallinity and the crystallite sizes, the annealing temperature has a small influence on the remanence for the same annealing time, however for the same annealing temperature the remanence tends to vary with annealing time. With increasing annealing time, the crystal structure of the hard phase is improved, which in turn improves the interphase exchange coupling. The stronger interphase exchange coupling leads to an increase in remanence with annealing time, Table 1.

As coercivity increases with annealing time, the remanence decreases. By milling, due to the decomposition of Nd$_2$Fe$_{14}$B phase, the α-Fe content increases in the composite. After annealing the Nd$_2$Fe$_{14}$B phase is progressively restored and there is a slight decrease of the remanence values with annealing time. The 6 h MM samples show both higher coercivity and remanence values compared to the ones obtained for the 8 h MM samples – Table 1.

3.2. INFLUENCE OF SOFT PHASE PRE-MILLING

In order to study the effect of dry pre-milling of the soft phase we prepared milled Nd$_2$Fe$_{14}$B/α-Fe nanocomposites with 4 h dry-milled Fe powder as the soft phase. The XRD patterns for the as-milled and annealed Nd$_2$Fe$_{14}$B/α-Fe samples are shown in Figure 5.
The XRD peaks of hard magnetic phase in nanocomposites prepared with pre-milled Fe almost disappear even after 2 h of milling, whereas in samples prepared with non pre-milled Fe, these peaks are still present for 2 h MM and are visible even after 4 h MM – Figure 1. This means that the crystal structure of the hard phase is destroyed much faster when using pre-milled Fe. During pre-milling, the Fe powder is mechanically hardened and, throughout the milling of the nanocomposite powder mixture, the hard phase will absorb more energy. After annealing, the crystal structure of Nd$_2$Fe$_{14}$B is recovered. However, the XRD peak intensities are much lower compared to the previous case where unmilled Fe powder was used. The mechanical hardening of Fe during milling is confirmed by the nanoindentation measurements. These measurements show a mechanical hardness value of 670 MPa for unmilled Fe and 840 MPa for dry pre-milled Fe. This behaviour is also confirmed by the SEM micrographs of the unmilled and pre-milled Fe samples, Figure 6. The Fe crystallite sizes for 6 h MM annealed samples containing dry pre-milled Fe appear to be smaller than in the case of using non pre-milled Fe, Fig. 7, however this variation is within the experimental errors. Also, a synthesis of the average crystallite sizes ($d$) for the 6 h MM annealed samples containing non pre-milled and dry pre-milled (dry PM) Fe is given in Table 2 along with coercive field ($\mu_0H_C$) and remanent magnetization values ($M_r$).
Fig. 6 – SEM micrographs for unmilled Fe (a) and 4 h dry pre-milled Fe (b).

Fig. 7 – Annealing time dependence of the average Fe crystallite sizes derived from XRD for the 6h MM and annealed samples containing dry pre-milled (dry PM) and non pre-milled Fe respectively.

The constituents’ distribution and the grain sizes on the annealed 6h MM Nd$_2$Fe$_{14}$B+10wt% Fe composite containing pre-milled Fe are shown in Figure 8. It can be seen that the samples are chemically homogeneous with identical distributions of Nd and Fe at the micrometric scale.
Table 2

Average α-Fe crystallite sizes ($d$), FWHM values of the α-Fe (211) XRD peak, coercive field ($\mu_0 H_c$) and remanent magnetization values ($M_r$) for the 6 h MM annealed samples containing non pre-milled and dry pre-milled (dry PM) Fe respectively

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<th>Milling time (h)</th>
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Fig. 8 – SEM image (a) and EDX analysis of the same area for Nd (b) and Fe (c) for the 6h MM Nd$_2$Fe$_{14}$B+10 wt% α-Fe sample containing dry pre-milled Fe, annealed at 750 °C for 2 min.
The demagnetization curves after magnetization at 10 T for the 
Nd$_2$Fe$_{14}$B + 10wt% Fe nanocomposite containing pre-milled Fe are shown in
Figure 9(a). When the remanence values increase, there is a substantial drop in
coercivity for the samples which contain pre-milled Fe – Table 2. This can be
attributed to the more energetic milling of the hard phase, which is not fully
restored after annealing. All of the samples containing dry pre-milled Fe have
slightly higher remanence values than the case where non pre-milled Fe was used.
Even though the soft phase crystallites appear to be smaller, the exchange coupling
in the case of nanocomposites containing pre-milled Fe is much weaker compared
to those containing non pre-milled Fe, Figure 9.

4. CONCLUSIONS

The magnetic behaviour of the 6 h MM short time annealed samples showed
a good soft/hard exchange coupling and high coercivity and remanence. The
coercivity increases with both annealing temperature and time due to the
progressive restoration of the Nd$_2$Fe$_{14}$B crystal structure, the maximum coercive
field value of 0.61 T being obtained for the sample annealed at 750 °C for
2 minutes. The remanence values decreased with annealing temperature/time due
to the progressively lower Fe content present in the sample caused by the
recombination of Nd$_2$Fe$_{14}$B.

The pre-milling of the soft phase led to slightly smaller α-Fe crystallites, but
it also caused a more pronounced damaging of the hard phase crystal structure.
This was correlated with the mechanical hardening of Fe as confirmed by
nanoindentation measurements. Iron pre-milling caused an incomplete recovery of Nd$_2$Fe$_{14}$B crystallinity after annealing, and consequently lower coercivities and higher remanence values.

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