Structural and Magnetic Properties of $Nd_2Fe_{14}B$/α-Fe Nanocomposites Obtained by Mechanical Milling and Short Time Annealing

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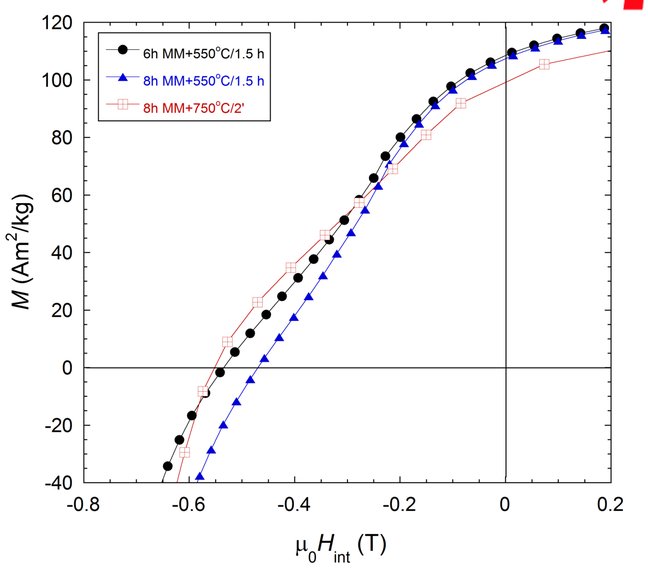
Abstract: This study presents the effect of different milling times and short time annealing on the structural and magnetic properties of $Nd_2Fe_{14}B$/10wt% Fe nanocomposites prepared by high energy ball milling. The XRD peaks of the hard magnetic phase disappear after milling due to the damaging of the $Nd_2Fe_{14}B$ crystal structure. After annealing, the characteristic peaks of the hard magnetic phase are restored with a limited growth of the soft magnetic phase crystallites. The magnetic behavior was investigated from hysteresis curves and d*M*/d*H* vs. *H* plots. The best exchange coupling was obtained for the 6 h milled sample annealed at 700 ˚C for 2 minutes with a maximum coercive field value of 0.44 T. Taking into account the milling and annealing conditions, the $Nd_2Fe_{14}B$/α-Fe exchange coupling is analyzed.

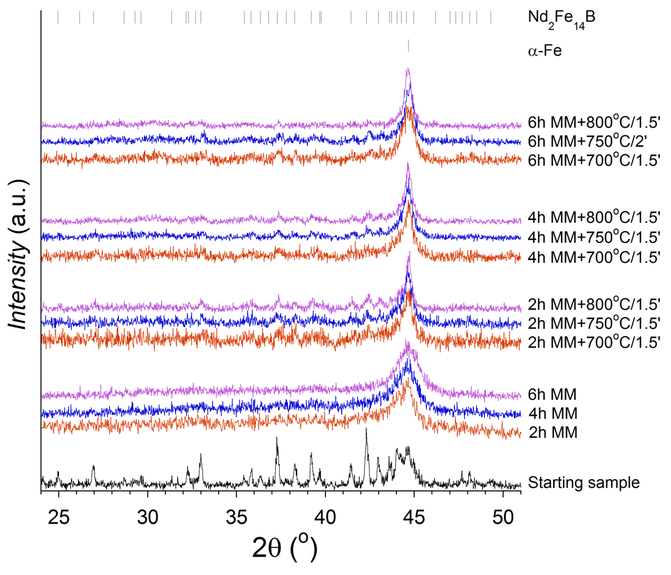
Experimental:

- The $Nd_2Fe_{14}B$ hard phase was prepared by induction melting in an Ar atmosphere, followed by annealing in vacuum at 950 ˚C for 68 h. The ingot was ground to a fine powder under 500 μm. The soft magnetic phase (12 g of NC 100.24 commercial Fe powder – Höganäs product) was milled with 5 ml benzene for 4 h in an inert Ar atmosphere with a ball to powder weight ratio of 10:1.
- The $Nd_2Fe_{14}B$ powder was mixed with the pre-milled Fe phase in a weight ratio of 90% $Nd_2Fe_{14}B$/10% Fe. The mixture was dry-milled in Ar for 2, 4 and 6 h respectively with a ball to powder weight ratio of 10:1. The milled samples were annealed in an Ar atmosphere at 700, 750 and 800 ˚ C for 0.5-2.5 min and quenched in water.
- X-Ray diffraction measurements were performed on a Brüker D8 Advance diffractometer using Cu K_α radiation.
- Magnetic measurements were carried out on powder samples fixed in epoxy resin using the extraction method at 300 K in applied fields up to ±10T. Assuming isolated spherical magnetic particles we used a demagnetization factor of 1/3 for magnetic data.



For ***classically annealed samples***, the interphase exchange coupling is better after 6 h MM compared to 8 h MM [1,2]. ***What will happen after short time annealing?***

Results and Discussions:



XRD: starting, as-milled and annealed $Nd_2Fe_{14}B$+10%Fe samples.

Damaging of the crystal structure and increased internal stress and defect density by MM.

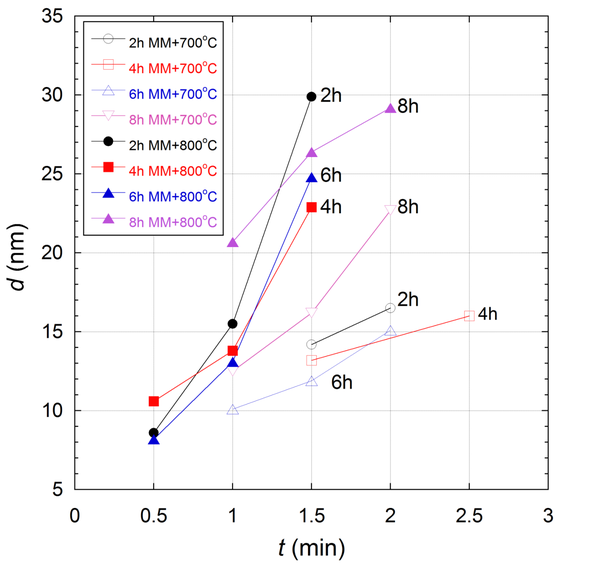
Hard phase XRD peaks disappear even after 2 h MM.

The $Nd_2Fe_{14}B$ crystal structure is restored after annealing.

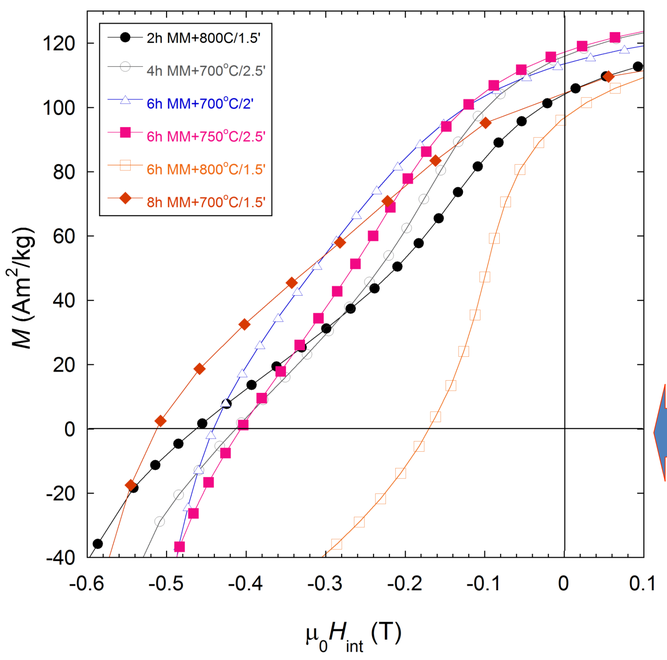
d ≈ 10-25 nm

No excessive growth of the soft phase crystallites during the ***short time annealing***.

The crystallite sizes of the annealed 6 h MM samples are smaller than those of the annealed 8 h MM samples [1].



Mean crystallite sizes of α-Fe vs. annealing time for the for the as-milled and annealed samples. The lines are guides for the eye.

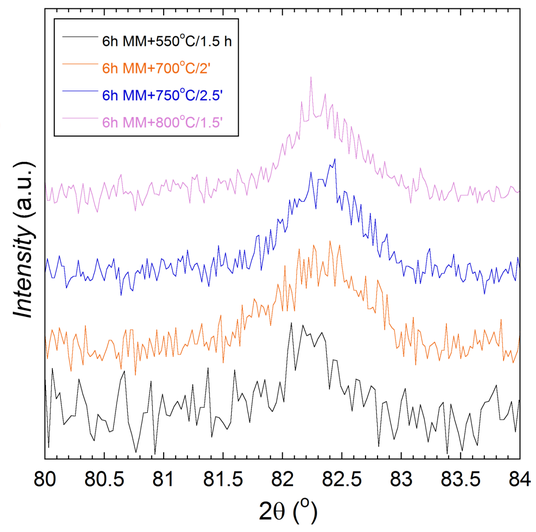


Demagnetization curves for $Nd_2Fe_{14}B$+10% wt. Fe samples 2, 4, 6 and 8 h MM short time annealed; ***$H_{int}=H_a-Ml3$.***

The crystallite sizes were determined using the Scherrer formula for the peak with $2\theta = 82.3$ ˚:

$$d = \frac{K\lambda}{\beta \cos\theta}$$

d is the average crystallite size, *K* is the shape factor, *λ* is the wavelength, *β* is the FWHM of the peak and *θ* is the Bragg angle.



XRD peaks centered at $2\theta = 82.3$ ˚ corresponding to α-Fe.

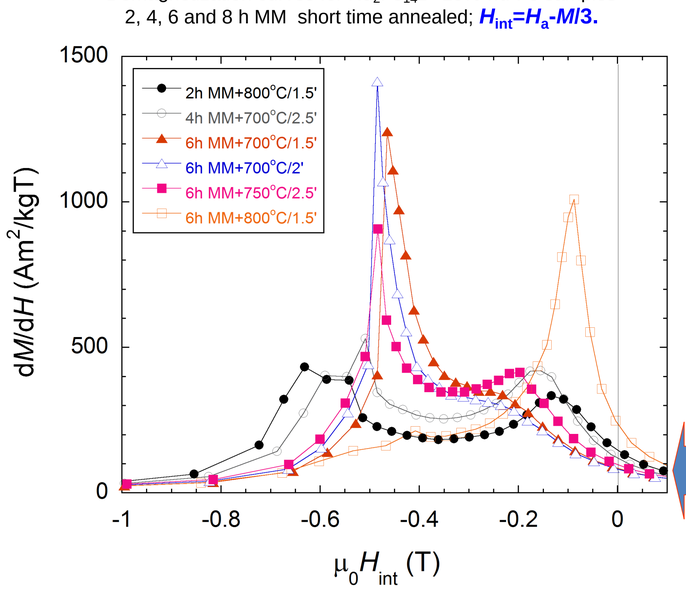
The coercivity of the short time annealed 6 h MM samples increases with annealing time.

Progressive restoration of the $Nd_2Fe_{14}B$ crystal structure.

Coercivity decreases with increasing annealing temperature ⇐ larger α-Fe crystallites.

Fe mean crystallite sizes (*d*), coercive field ($\mu_0 H_c$) and remanent magnetization values (M_r) for the $Nd_2Fe_{14}B$+10 wt% Fe 6 h MM annealed samples.

Milling time (h)	Annealing temperature (˚C)	Annealing time (min)	*d* (nm)	$\mu_0 H_c$ (T)	M_r (Am²/kg)
6	700	1.5	10	0.42	114
		2	15	0.44	114
	750	2	20	0.38	124
		2.5	21	0.41	117
	800	1.5	25	0.17	97
	550 [3]	90	34	0.55	115
8 [1]	700	1.5	16	0.51	103
	800	1.5	26	0.54	96

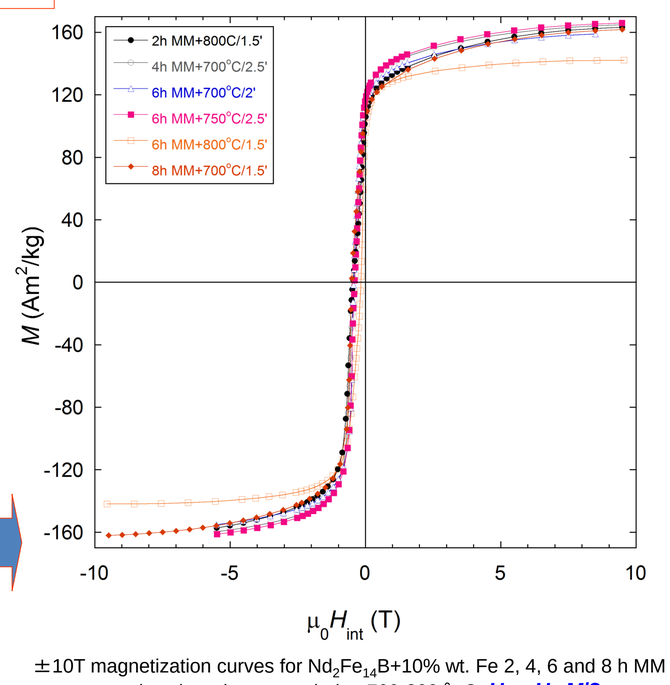


dM/dH vs. *H* curves for $Nd_2Fe_{14}B$+10% wt. Fe samples 2, 4, and 6 h MM short time annealed; ***$H_{int}=H_a-Ml3$.***

Low field peaks ⇒ badly coupled/uncoupled α-Fe

Higher field peaks ⇒ exchange-coupled nanocomposite.

Saturation is not reached up to 10 T.



±10T magnetization curves for $Nd_2Fe_{14}B$+10% wt. Fe 2, 4, 6 and 8 h MM samples short time annealed at 700-800 ˚ C; ***$H_{int}=H_a-Ml3$.***

Progressive decoupling with increasing annealing time/temperature.

Increasingly larger soft phase crystallites and possible phase alterations.

Conclusions:

- ***Short time annealing restores the structure of the hard phase*** destroyed by milling with a ***limited growth of the soft magnetic crystallites***.
- The exchange ***coupling strength*** increases with milling time possibly due to ***smaller soft phase crystallites*** and a better homogeneity of the mixture.
- The ***best exchange coupling*** was obtained for the ***6 h MM*** sample annealed at ***700 ˚C for 2 minutes*** with a maximum coercive field value of ***0.44 T***.
- The ***coercivity*** of the short time annealed 6 h MM samples is ***slightly lower*** than previously reported values on the classically annealed 6 h and short time annealed 8 h MM samples, however, they show a ***higher remanence***.
- The diminishing of the coercivity could be attributed to the pre-milling of the soft phase with benzene.

[1] V. Pop, S. Gutoiu, E. Dorolti, O. Isnard and I. Chicinaş, *J. Alloys Compd.,* **509**, 9964 (2011).
[2] V. Pop, S. Gutoiu, E. Dorolti, C. Leostean, O. Isnard, I. Chicinas and O. Pana, *J. Alloys Compd.,* **581**, 821 (2013).
[3] S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinaş, and V. Pop, *J. Optoelectron. Adv. Mater.,* **12**, 2126 (2010).

Acknowledgment
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