Influence of Milling Conditions on the Hard/Soft Exchange Coupling of the Short Time Annealed $Nd_2Fe_{14}B$/α-Fe Nanocomposite

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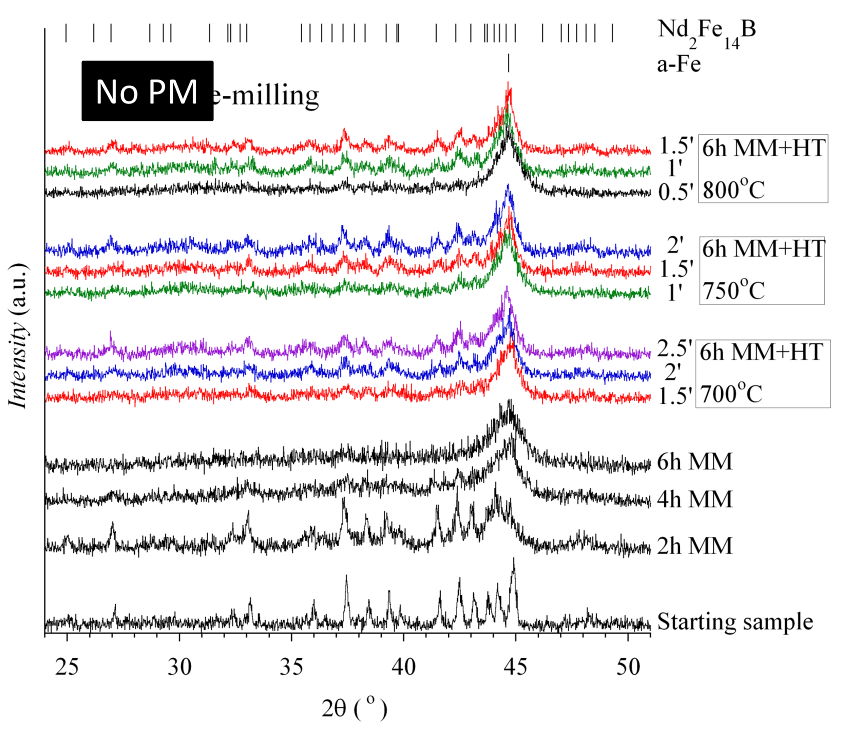
Abstract:

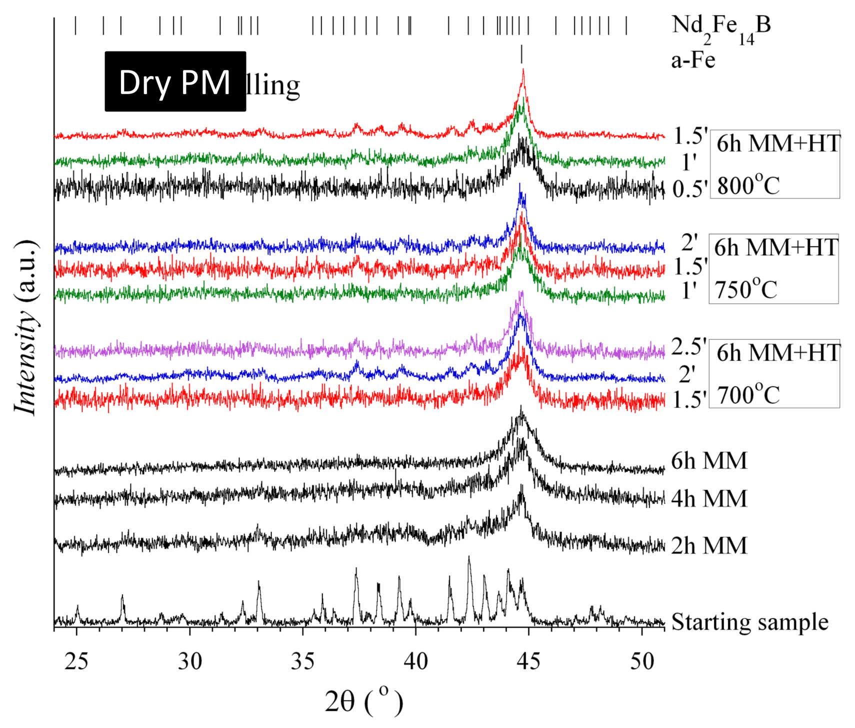
The effects of short time annealing and soft phase pre-milling on the structural and magnetic properties of 6 h milled $Nd_2Fe_{14}B$/10wt% Fe magnetic nanocomposites were investigated. The XRD peaks of $Nd_2Fe_{14}B$ progressively disappeared after milling due to crystal structure damage, this effect being more pronounced when using pre-milled Fe (PM). After annealing, the characteristic peaks of $Nd_2Fe_{14}B$ were restored with a limited growth of the α-Fe crystallites.The magnetic behavior was investigated using hysteresis curves and d*M*/d*H* vs. *H* plots. The best exchange coupling was obtained for the samples which contain ~~non pre-milled~~ unmilled Fe as the soft phase, with a maximum coercive field value of 0.61 T. The samples containing pre-milled Fe have lower coercive field values, but show a higher remanence. 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 magnetic phase was prepared by induction melting in a purified Ar atmosphere, followed by annealing in vacuum at 950 ºC for 68 h. The ingot was ground to a fine powder under 500 µm. The soft magnetic phases consisted of NC 100.24 commercial Fe powder – Höganäs product and Fe powder milled for 4 h under Ar in a high-energy planetary mill (Fritsch Pulverisette 4) with a ball to powder weight ratio of 10:1.
- The $Nd_2Fe_{14}B$ powders were mixed with the two soft phases in a weight ratio of 90% $Nd_2Fe_{14}B$+10% Fe. The two mixtures were 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 ºC for 0.5-2.5 min and were quenched in water.
- X-Ray diffraction measurements were performed on a Brüker D8 Advance diffractometer using Cu K_α radiation.
- 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 AFM equipped with a XE 70 TD 21562 Sapphire Cantilever nanoindentor with a diamond tip, the data being interpreted using the Oliver and Pharr model.
- Magnetic measurements were carried out on powder fixed in epoxy resin 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.

Results and Discussions:





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

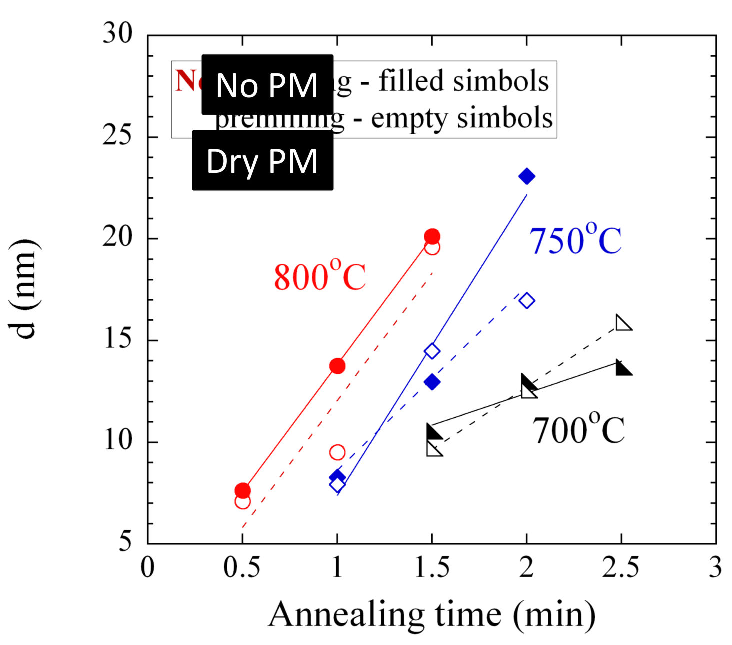
When using pre-milled Fe the XRD peaks corresponding to the hard phase almost disappear even after 2 h of milling

The crystal structure of the hard phase is destroyed much faster when using pre-milled Fe.

The crystallite sizes were determined from the Fe XRD peak at $2\theta = 82.3°$

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

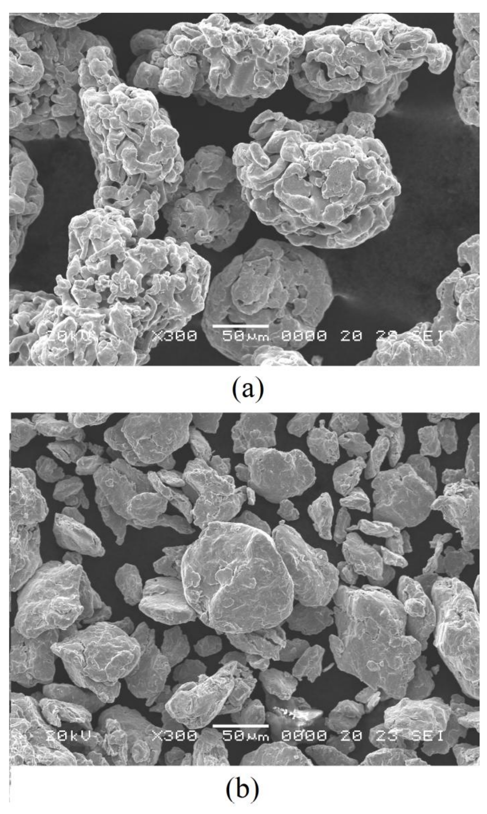
d (nm) is the average crystallite size



The soft phase crystallite sizes of the 6 h MM annealed samples, which contain dry pre-milled Fe, are slightly smaller than those obtained for 6 h MM samples containing non pre-milled Fe.

d ~ 5 - 25 nm

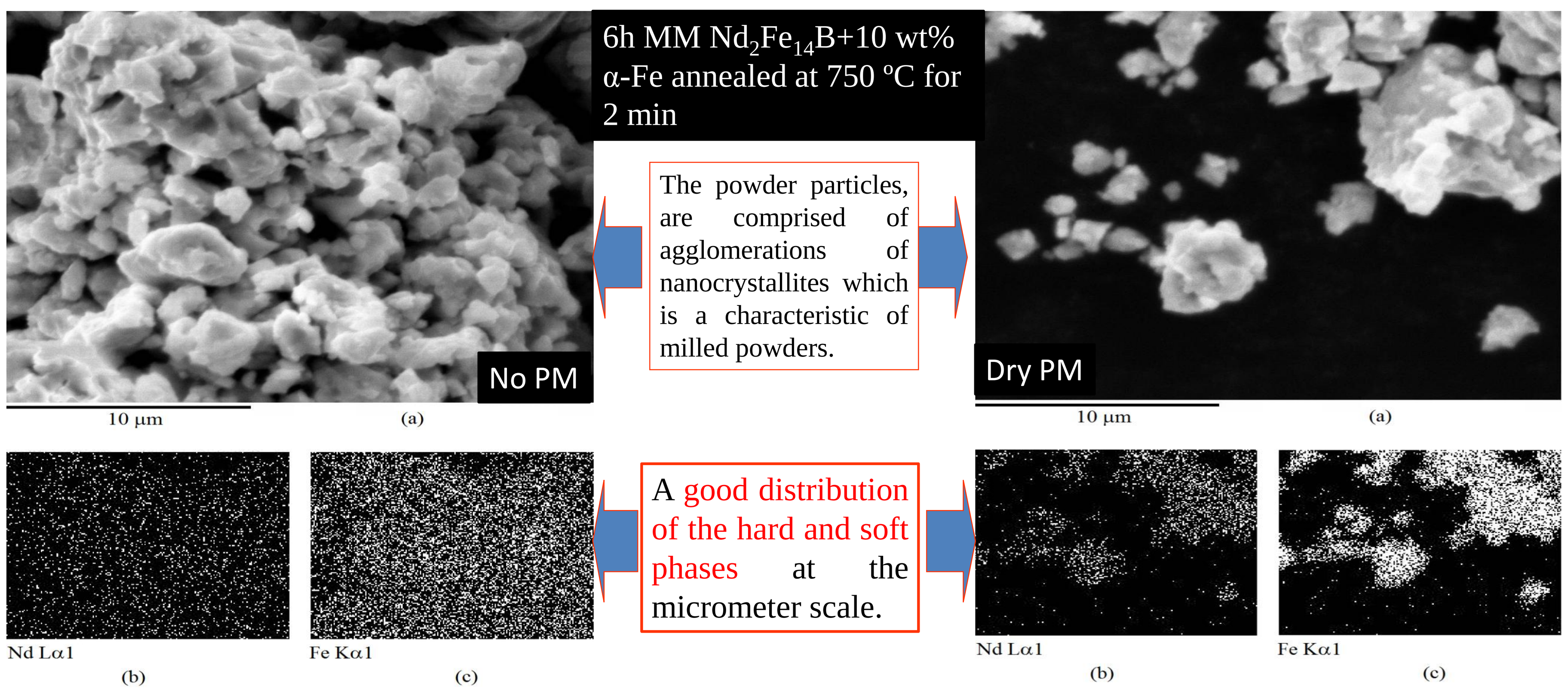
average crystallite sizes are small enough for a good ~~interphone~~ interphase exchange coupling



SEM micrographs for un-milled Fe (a) and 4 h dry pre-milled Fe (b).

Measurements have shown that the pre-milled Fe (PM) is significantly harder than the un-milled powder. This is due to the cold ~~working~~ welding which occurs during the milling process.

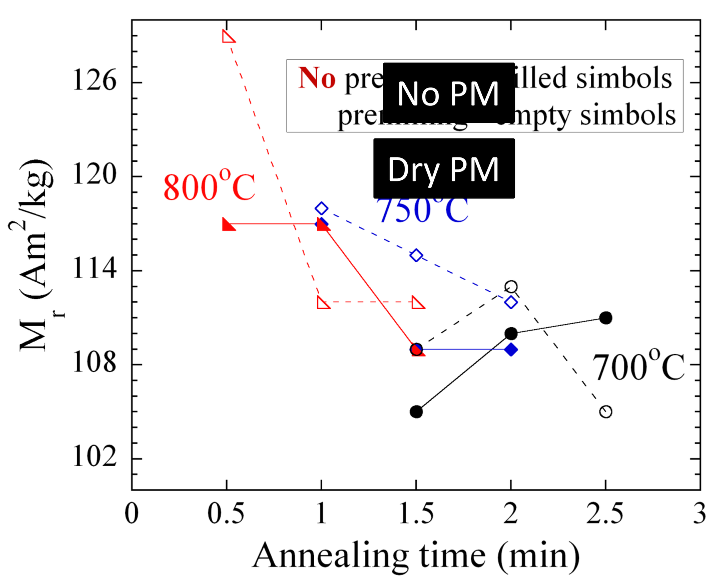
Pre-milled Fe shows smaller and more compact particles than un-milled Fe.



The powder particles, are comprised of agglomerations of nanocrystallites which is a characteristic of milled powders.

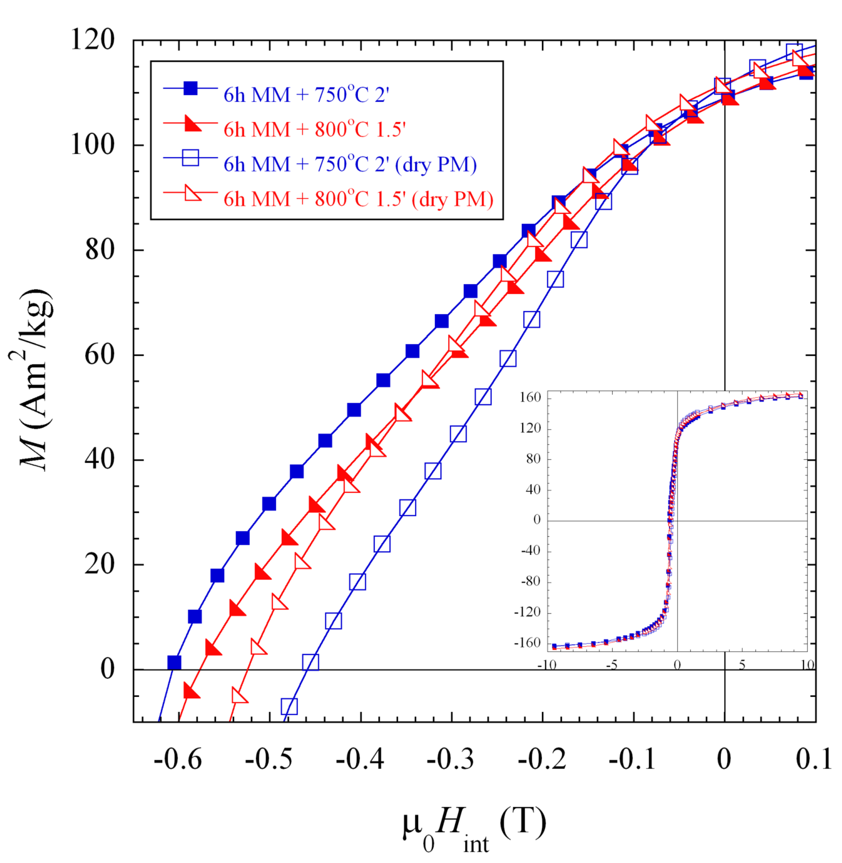
A good distribution of the hard and soft phases at the micrometer scale.

SEM image (a) and EDX analysis of the same area for Nd (b) and Fe (c)



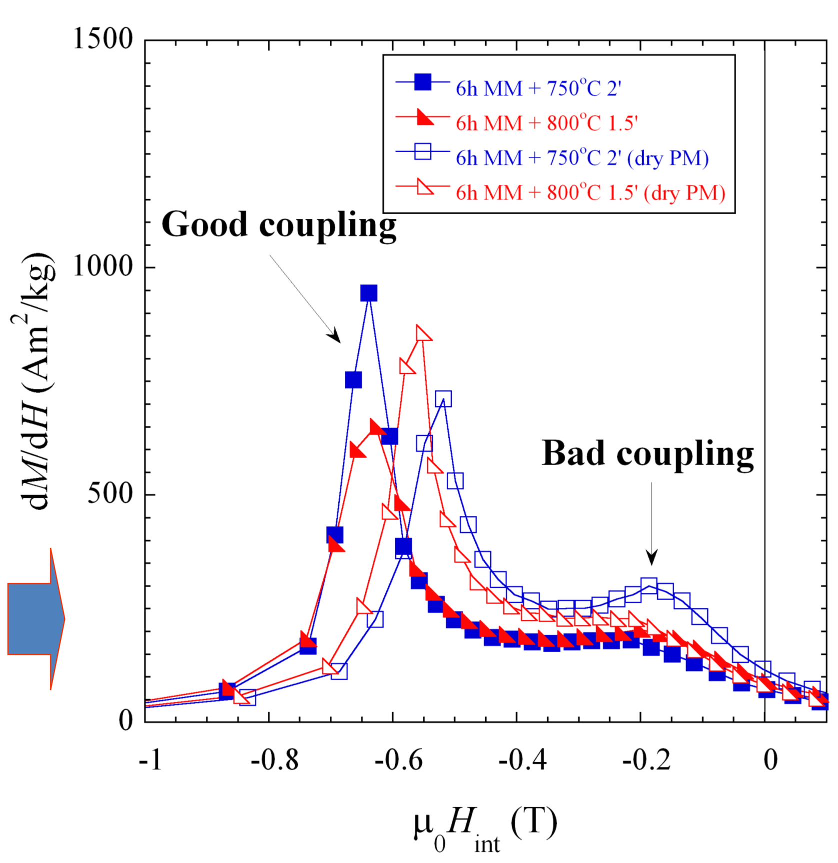
The higher remanence of the samples containing pre-milled Fe can be explained if we consider that they contain a higher quantity of segregated Fe.

During the milling process, some Fe segregates from the $Nd_2Fe_{14}B$ phase [1].

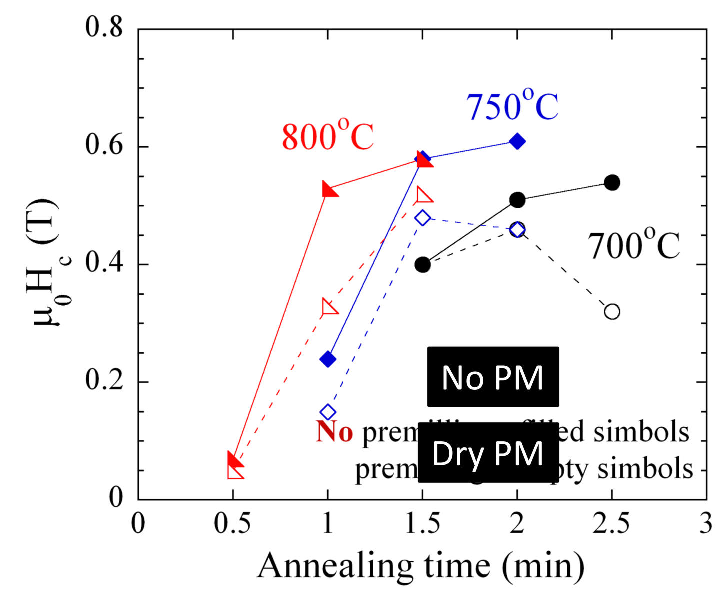


Pre-milled Fe increases the amount of damage to the crystalline structure of $Nd_2Fe_{14}B$, and thus leads to a decreased magnetic performance of the nanocomposites.

The annealed samples containing unmilled Fe show an efficient coupling between the hard and soft phases.



The samples containing pre-milled Fe present lower coercivity values, due to the more damaged crystalline structure of the hard magnetic phase.



Conclusions:

- XRD and SEM-EDX investigations have pointed out that while soft phase pre-milling may lead to slightly smaller α-Fe crystallites, ~~resulting~~ this results in a more pronounced damaging of the hard phase crystal structure during ~~the~~ milling.
- The magnetic behaviour of the 6 h MM short time annealed samples showed an efficient soft/hard exchange coupling.
- It was shown that coercivity increases with both annealing temperature and time due to the progressive restoration of the $Nd_2Fe_{14}B$ crystal structure, with a maximum coercive field of 0.61 T being obtained for the sample annealed at 750 ºC for 2 minutes.
- It was shown that Fe pre-milling weakens the soft/hard exchange coupling and decreases coercivity, however, Fe pre-milling increases remanence values.

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