Effect of Milling and Annealing Conditions on the Interphase Exchange Coupling of $Nd_2Fe_{14}B/\alpha$-Fe Magnetic Nanocomposites

Sever Mican, Răzvan Hirian, Viorel POP
Babeş-Bolyai University, Faculty of Physics, 400084 Cluj-Napoca, Romania

Olivier ISNARD
Institut Néel, CNRS, Joseph Fourier University, BP 166X, 38042 Grenoble, Cédex 9, France

Ionel CHICINAŞ
Materials Sciences and Engineering Dept., Technical University of Cluj-Napoca, 103-105 Muncii ave., 400641 Cluj-Napoca, Romania

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PN-II RU-TE-2011-3-0048

Outline

- **Introduction**
- **Experimental details**
- **Structure and microstructure**
- **Inter-phase magnetic coupling**
- **Conclusions**

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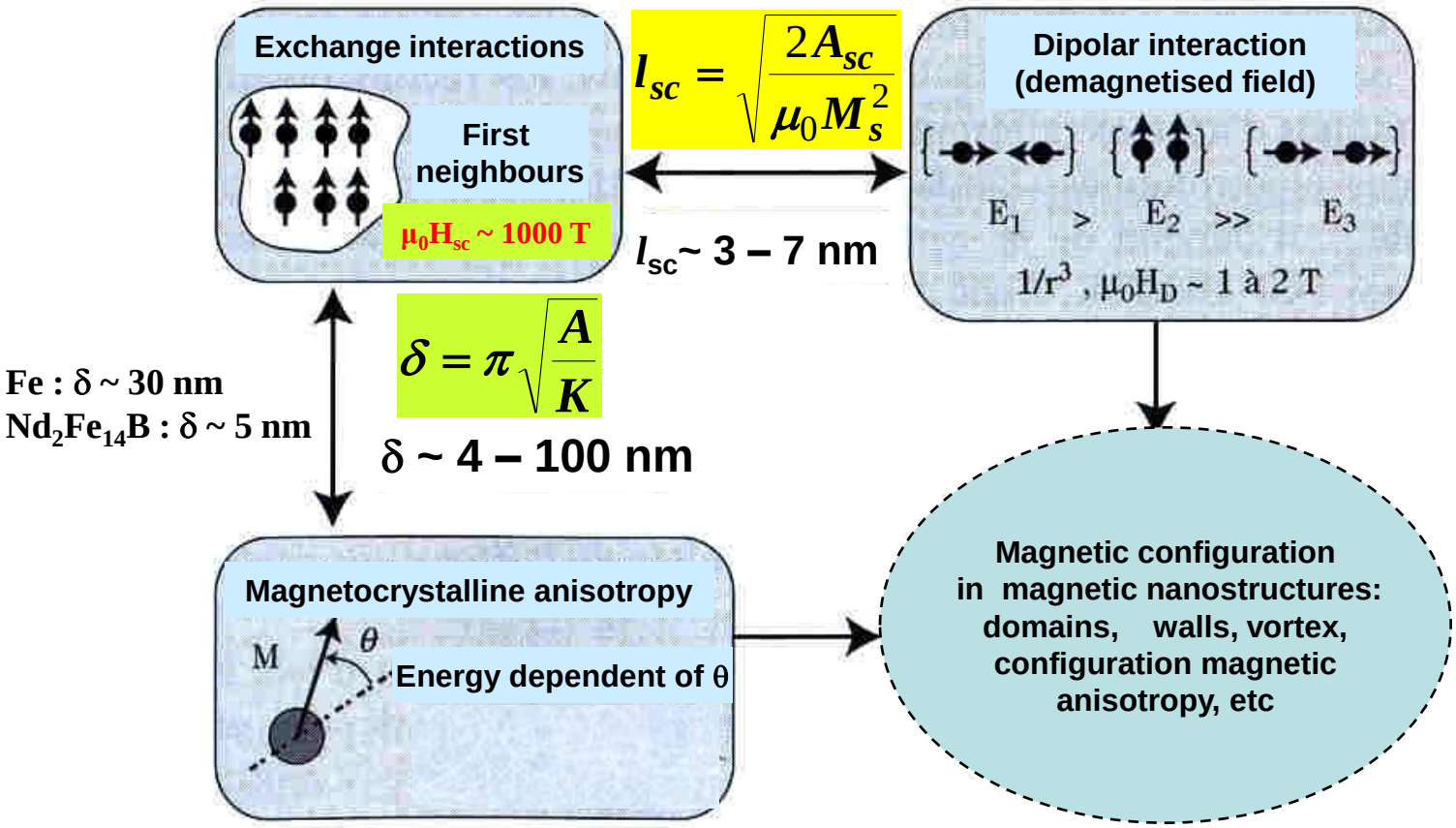
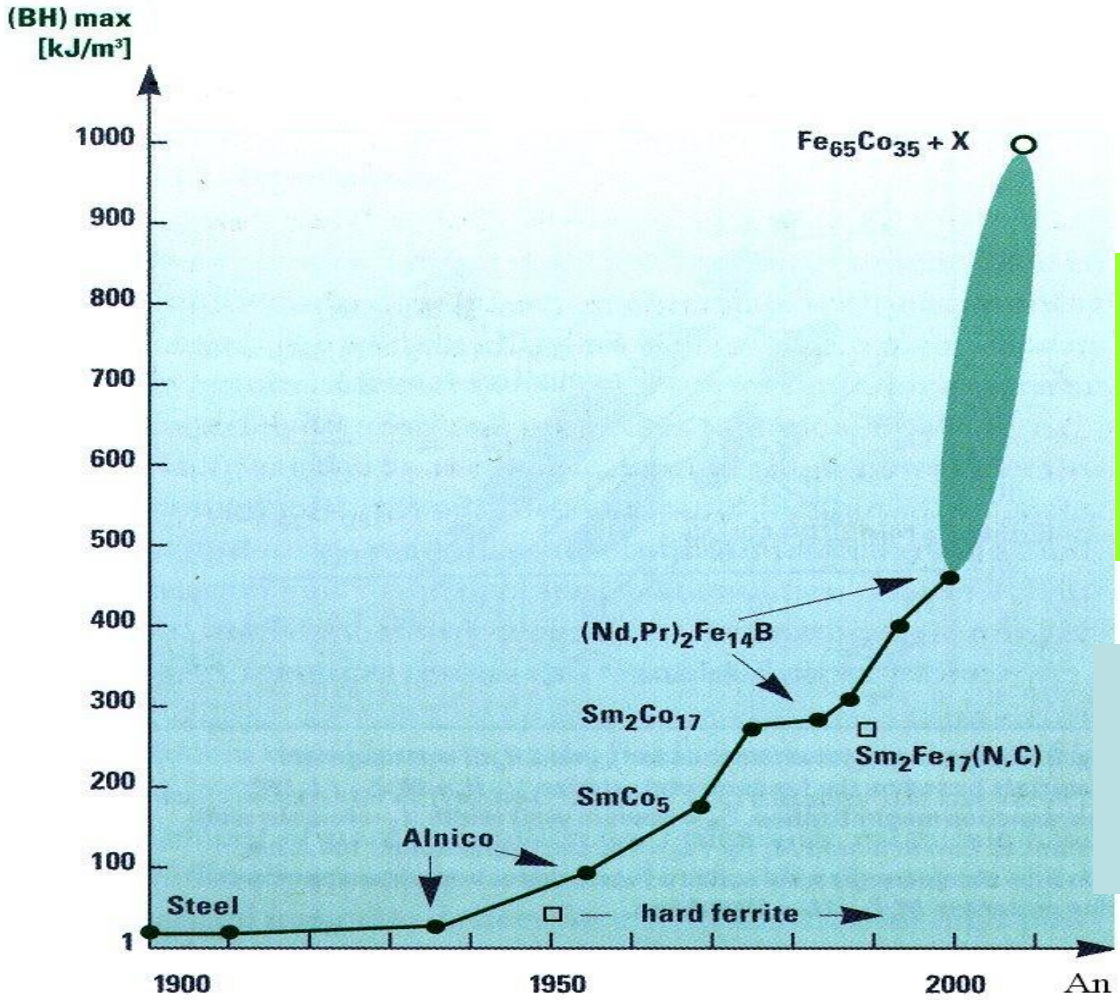
Nanophased materials behave differently from their macroscopic counterparts because **their characteristic sizes** are **smaller than the characteristic length scales** of physical phenomena occurring in bulk materials.



E. De Lacheisserie (edit.), Magnetisme, Presses Universitaires de Grenoble, 1999.

Theoretical predictions:



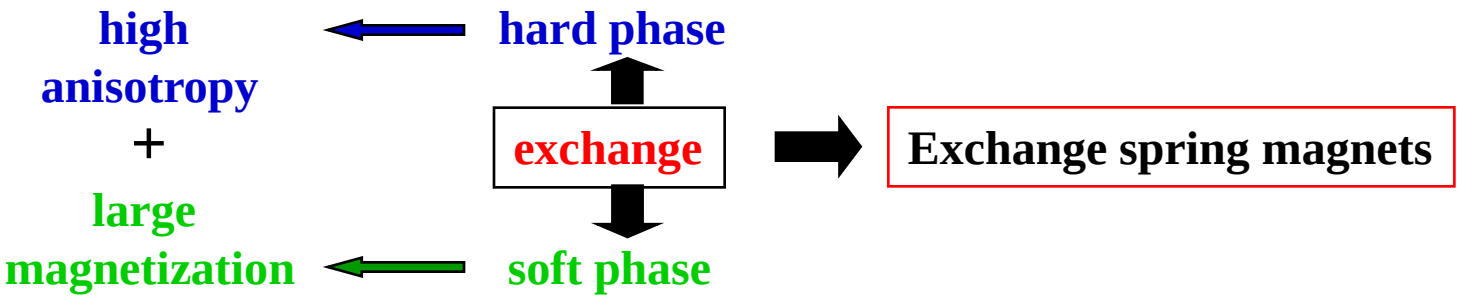
Best magnets on the market:
$(BH)_{max} \approx 500$ kJ/m3

$(BH)_{max} = 1090$ kJ/m^3 for nanostructured multilayers $Sm_2Fe_{17}N_3/Fe_{65}Co_{35}$

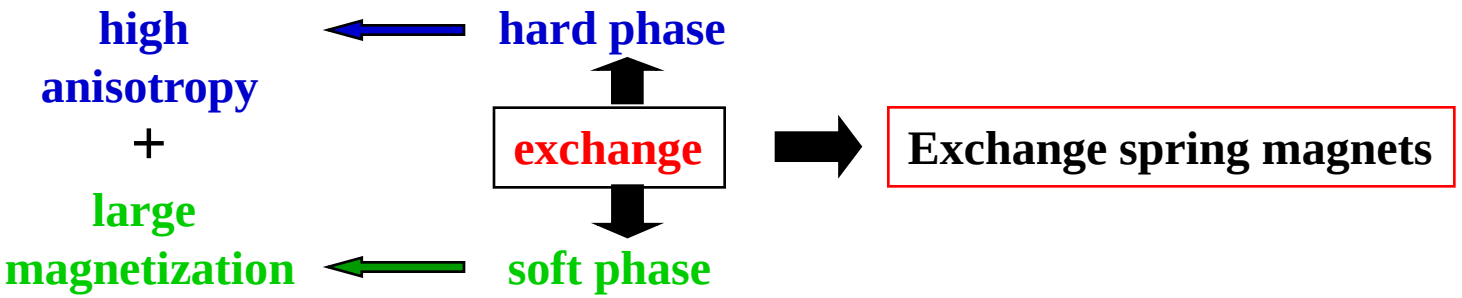
R. Skomski, J. Appl. Phys. 76 (1994) 7059

Kronmuller & Coey *Magnetic Materials*, in *European White book on Fundamentel Research in Materials Science* Max Planck Inst. Metallforschung, Stuttgart, 2001, 92-96

Experimental realisations: ??????????


high
anisotropy
+
large
magnetization
hard phase
exchange
soft phase
Exchange spring magnets

Structure
Microstructure → **Soft-hard exchange hardness**



$$D_{cr} \approx 2d_h$$

$$\delta_h = \pi\sqrt{A_h / K_h}$$

D_{cr} = **soft phase critical dimension**
δ_h = width of domain wall in the hard phase
A_h and K_h are the exchange and anisotropy constants

Nanocomposites prepared by mechanical milling (MM)

- **hard magnetic phases of $Nd_2Fe_{14}B$**

- **soft magnetic phases of α-Fe (10 wt%)**

Different milling energy:

1. **Different milling balls: Φ 10 mm and 15 mm**
2. **Different milling time: 6 h and 8 h of MM**

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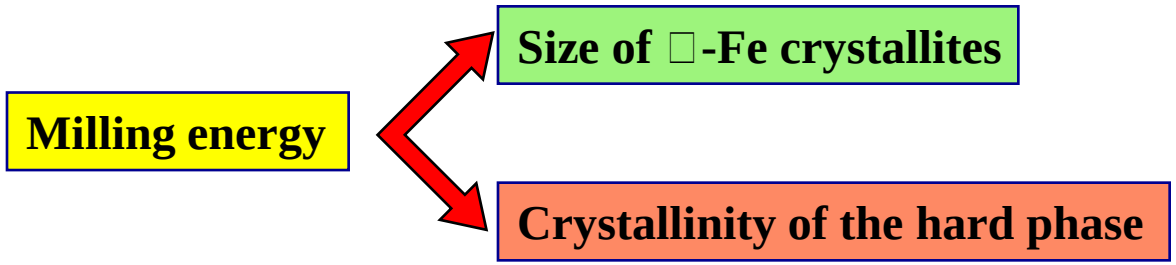

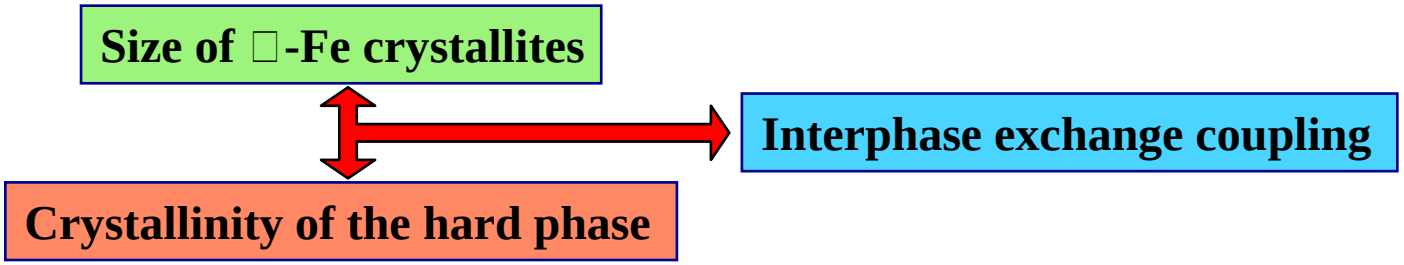

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Material preparation

- milling of the powders in a high energy planetary mill
- heat treatments (temperatures and duration)

Starting materials :

- hard magnetic phases of:
  $R_2Fe_{14}B$, ingots – prepared by melting
- soft magnetic phases of:
  Fe NC 100.24 powder (Höganäs), (< 40 μm)


Fritsch Pulverisette 4

Mechanical milling experiments:

- hard magnetic phases– crushed under 500 μm
- hard + soft magnetic powders– milled in Ar atmosphere for 2 – 8 h

Annealing:

- short time annealing: in argon/700, 750 or 800 ° C for 0.5 to 3 min.

Some previous studies:

By ***Mössbauer spectroscopy*** we detected an ***inter-diffusion*** between the two phases during milling or annealing*

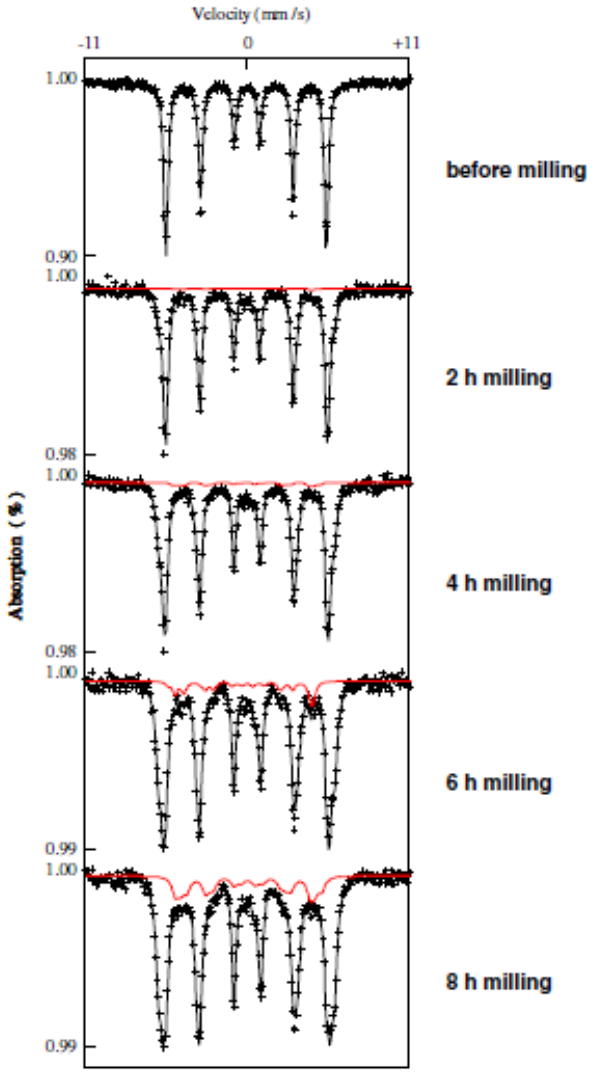


Figure 3. Room temperature Mössbauer spectra of the $SmCo_5$/Fe powder before milling and after milling for the indicated times. The contribution of the $Sm(Co,Fe)_5$ phase is displayed.

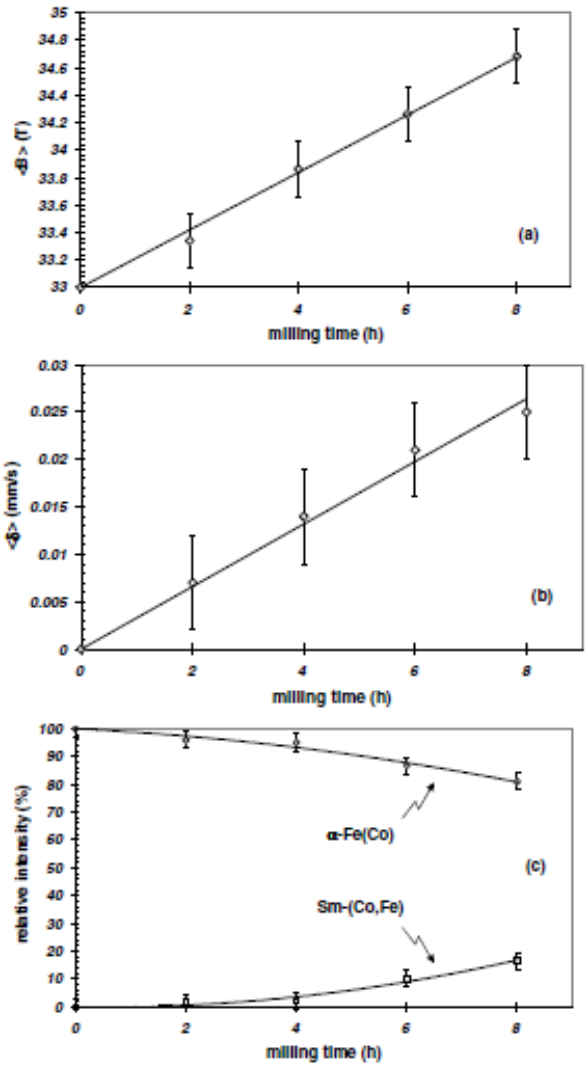
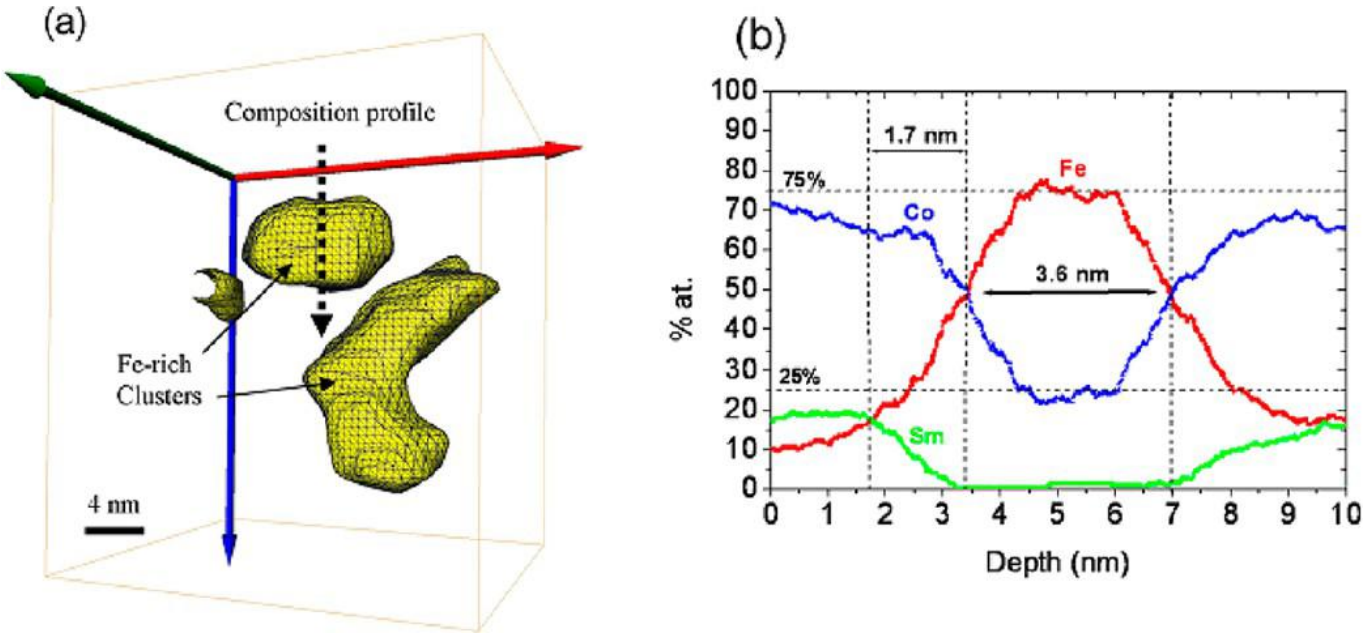


Figure 4. Evolution with the milling time of (*a*) the mean hyperfine field of the α-Fe(Co) contribution, (*b*) the mean isomer shift of the α-Fe(Co) contribution and (*c*) the relative intensities of the α-Fe(Co) and $Sm(Co,Fe)_5$ contributions. The lines are guides for the eye.

*J M Le Breton, R Lardé, H Chiron, V Pop, D Givord, O Isnard and I Chicinaş, J. Phys. D: Appl. Phys. 43 (2010) 085001

Some previous studies:

Atom probe tomography (APT) suggested that the observed Fe/Co ***inter-diffusion*** is initiated during the milling process and further increased by the annealing treatments.*



Nanoscale analysis of the $SmCo_5$/Fe powder milled for 8h:

(a) 3D image of Fe-rich clusters

(b) Concentration profile through a Fe-rich cluster along the black dashed arrow in panel (a).

*R. Lardé, J-M. Le Breton, A. Maître, D. Ledue, O. Isnard, V. Pop and I. Chicinaş, J. Phys. Chem., 117 (2013) 7801

Material characterisation

- X-ray diffraction (XRD)
- DSC measurements
- Magnetic measurements

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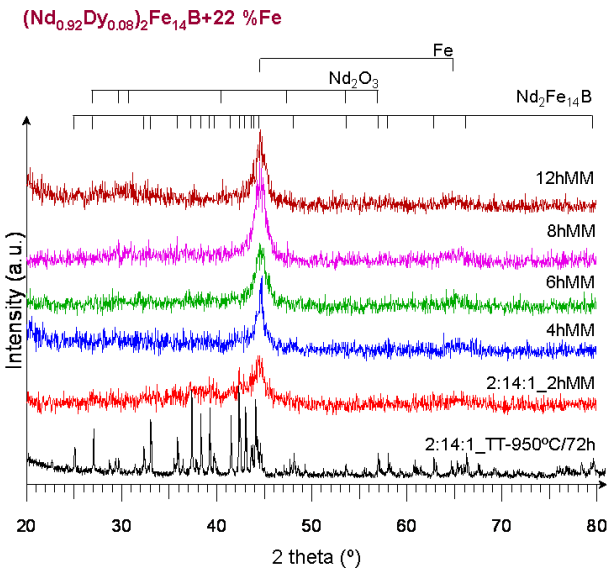
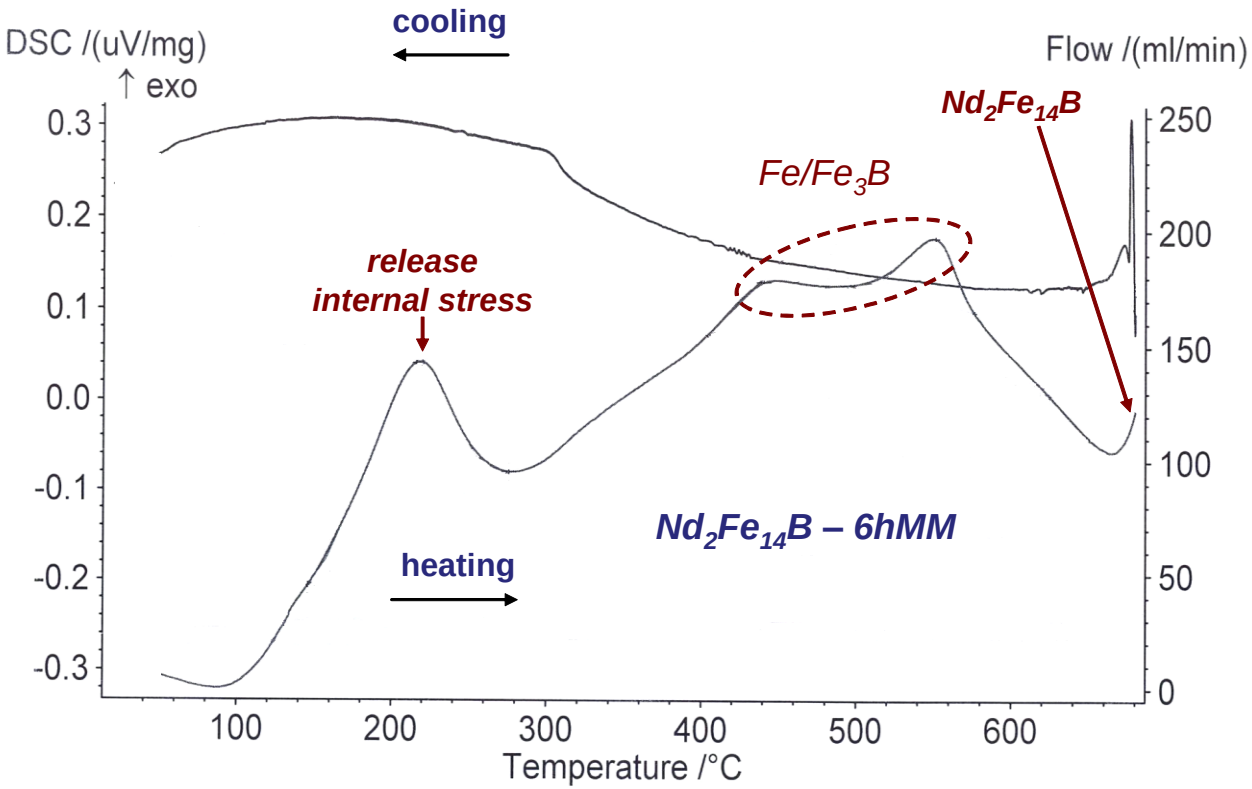
•The milled powders present poor crystallinity and a high defect density.

•The recrystallization temperature of the soft magnetic phase is smaller than the recrystallization temperature of the hard magnetic phases.

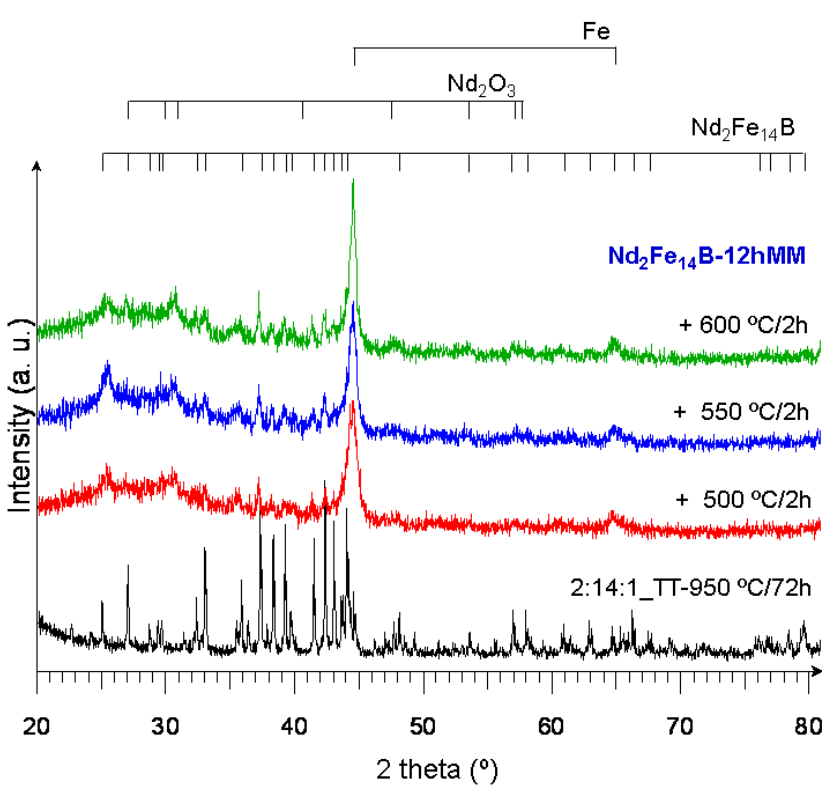
•By annealing we intended to recover the crystallinity of the hard phase and, in the same time, to hinder the growth of Fe crystallites during annealing.

•In order to complete both objectives simultaneously, a good crystallinity for the hard phase and fine crystallite (smaller than 20 nm) for Fe phase, we also investigate the effects of short time annealing (0.5 to 3 min at 700, 750 and 800 ° C) on the structure, microstructure and magnetic properties of the hard/soft $Nd_2Fe_{14}B/\alpha$-Fe magnetic composite.

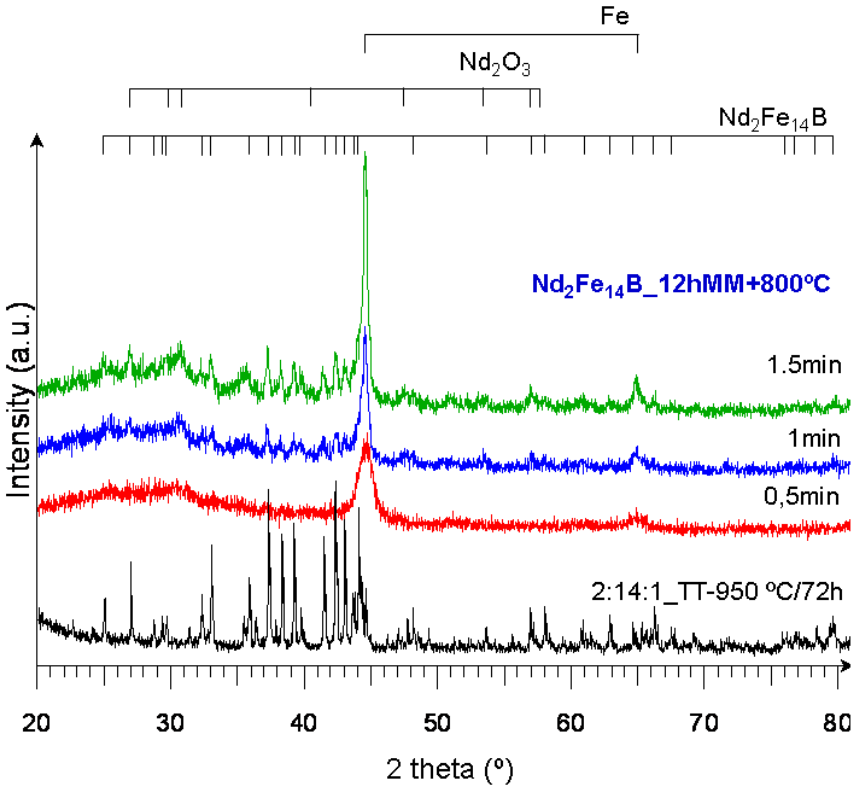




X-ray diffraction



Classical annealing
(450-650 ° C for 0.5 up to 10 h)



Short time annealing
(700, 750 or 800 ° C for 0.5 to 3 min)

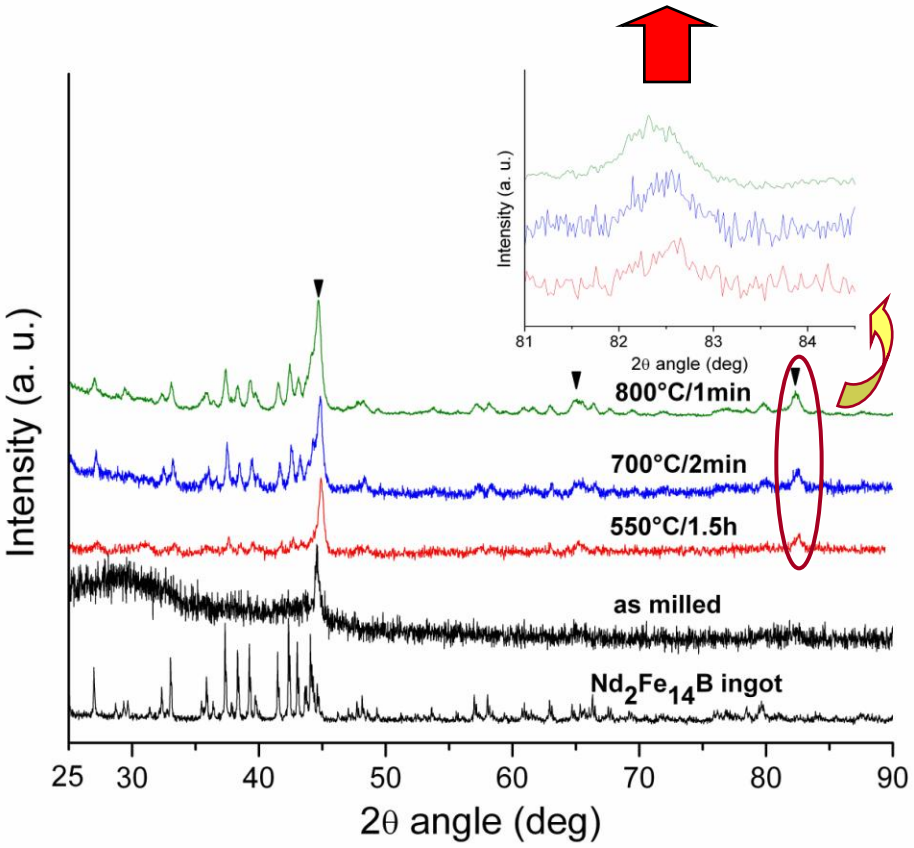
S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinas, V. Pop, J. Optoelectron. Adv. Mater. 12 (2010) 2126-2131

Annealing temperature (ºC)	Annealing time (min)	FWHM (º)	D (nm) α-Fe
700	1.0	0.88	12 (±2)
	1.5	0.77	14 (±2)
	2.0	0.66	16 (±2)
800	1.0	0.61	17 (±2)
	1.5	0.50	21 (±2)
	2.0	0.43	25 (±2)
550	90	0.40	26 (±2)

Annealing temperature (ºC)	Annealing time (min)	D (nm) α-Fe
700	1.0	15 (±2)
	1.5	19 (±2)
	2.0	24 (±2)
750	1.0	19 (±2)
	1.5	22 (±2)
	2.0	28 (±2)
800	1.0	24 (±2)
	1.5	27 (±2)
	2.0	30 (±2)
450	90	14 (±2)
550	90	26 (±2)
650	90	38 (±2)

$Nd_2Fe_{14}B$ + 22 % α-Fe

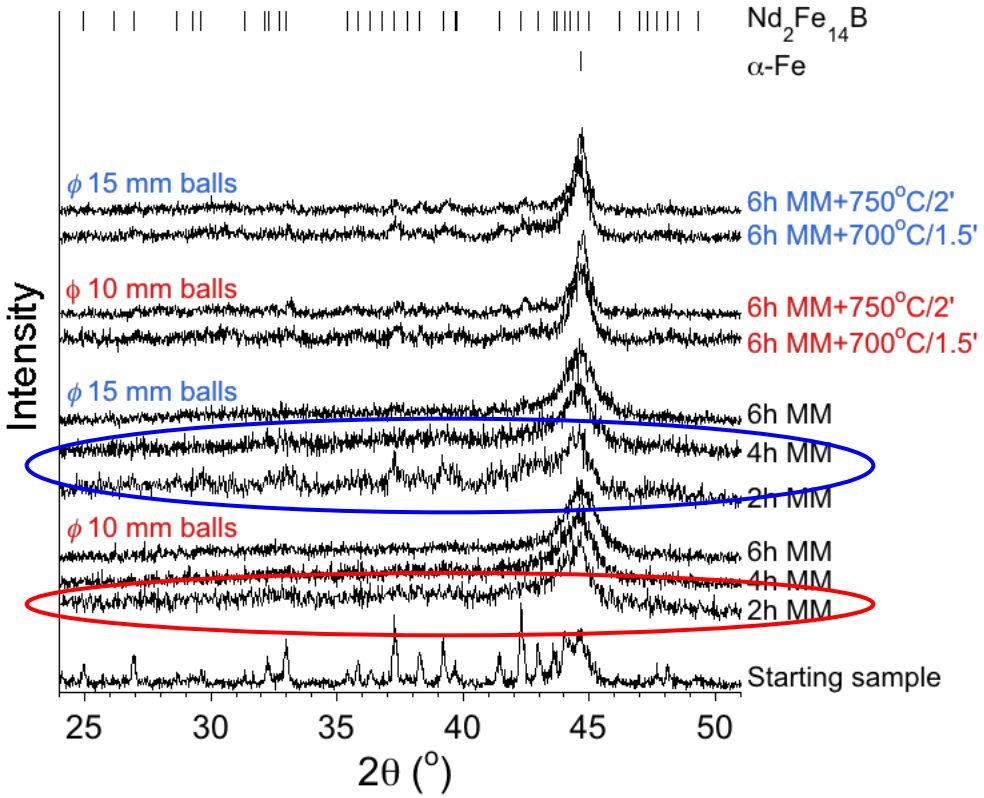
V. Pop et al, J. Alloys Compd. 581, 821-827 (2013).



$Nd_2Fe_{14}B$ + 10 % α-Fe

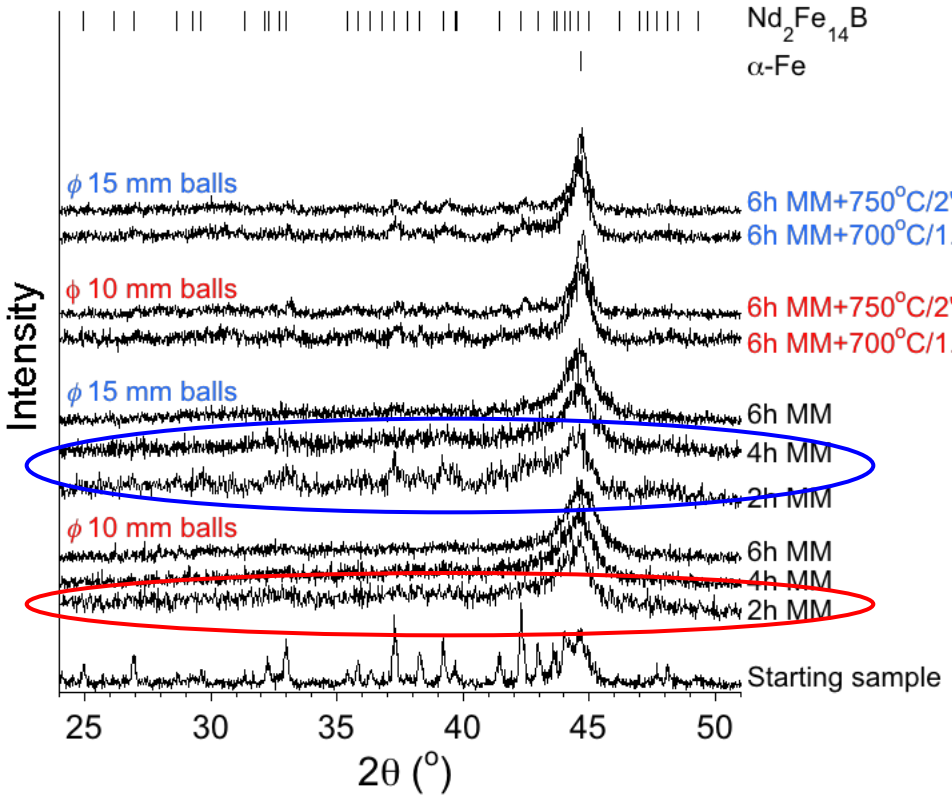
8h MM

V. Pop, S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinaş, J. Alloys Compd. 509, 9964-9969 (2011)



Different diameters of the milling balls

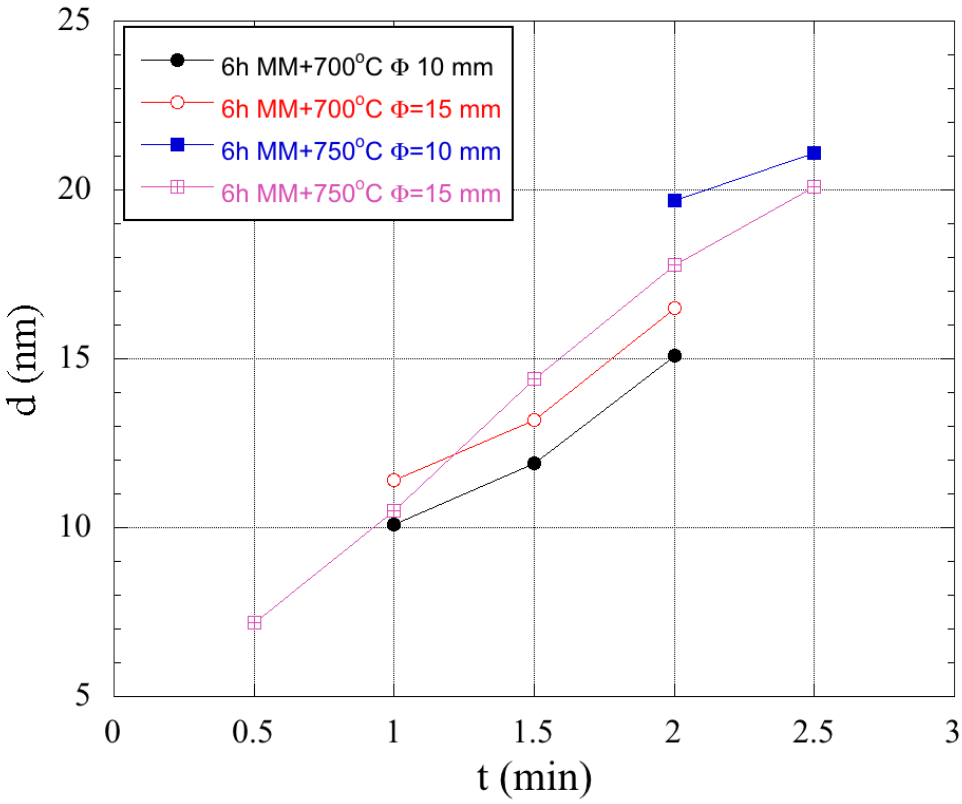
Different energy of milling



Milling time (h)	Annealing temperature (°C)	Annealing time (min)	*d* (nm)
6 (Ø 10 mm)	700	1.5	10
	750	2	15
		2	20
		2.5	21
	800	1.5	25
6 (Ø 15 mm)	700	2	17
	750	2.5	20
6	550 [10]	90	34
8 [7]	700	1.5	16
	800	1.5	26

Different diameters of the milling balls

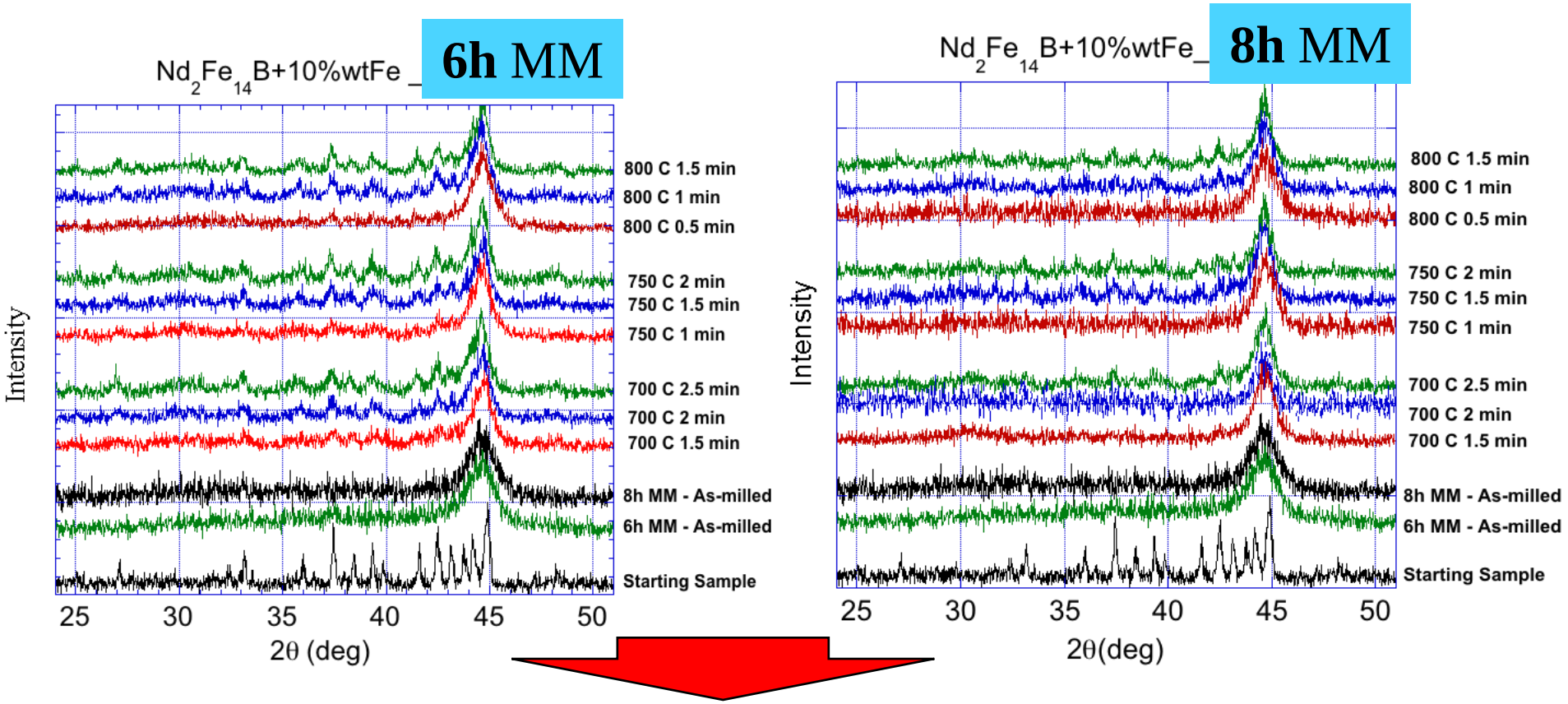
Different energy of milling



[7] V. Pop, S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinaş, *J. Alloys Compd.*, *509*, 2011, 9964.
[10] S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinaş, V. Pop, *J. Optoelectron. Adv. Mater.*, *12*, 2010, 2126.

Different times of milling

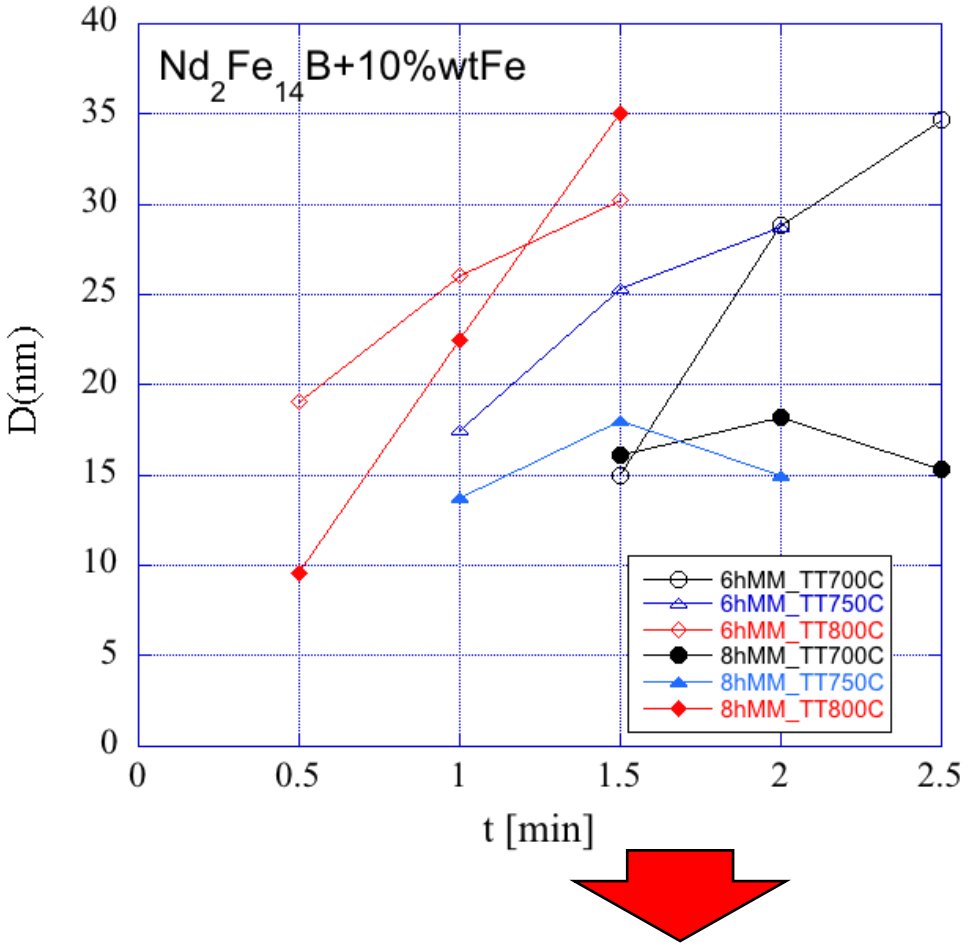
Different energy of milling



Better crystallinity for 6 h MM

Different times of milling

Different energy of milling



Smaller crystallites for 8 h MM

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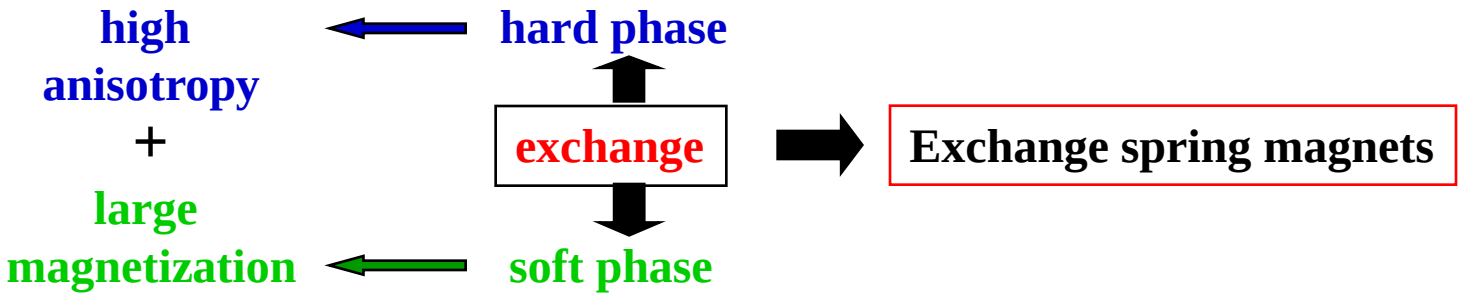
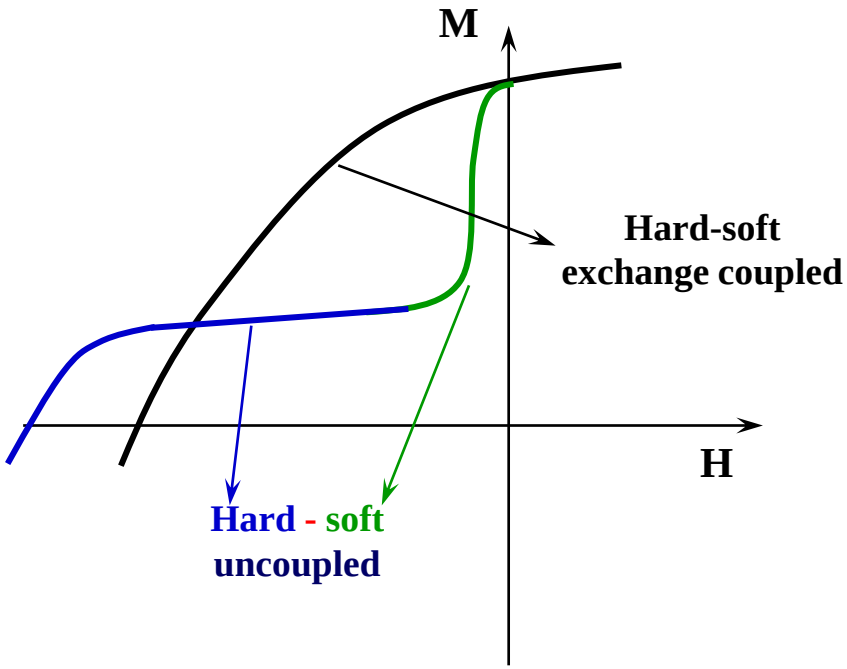
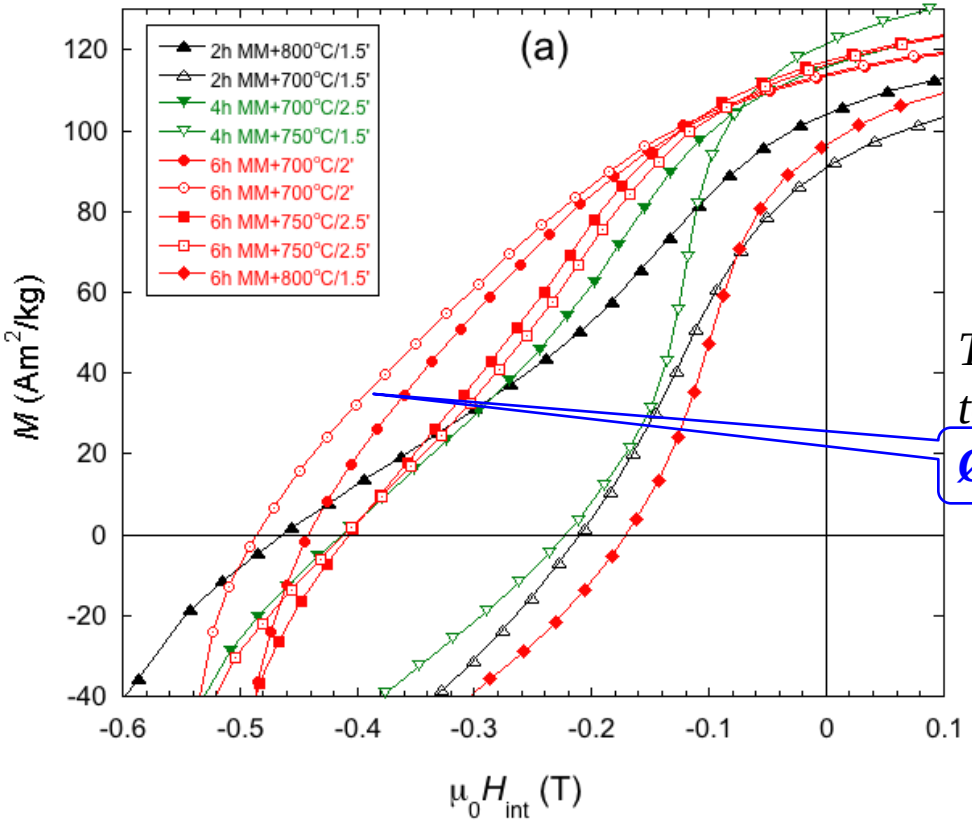

high
anisotropy
+
large
magnetization
hard phase
exchange
soft phase
Exchange spring magnets


M
H
Hard-soft
exchange coupled
Hard - soft
uncoupled



Different diameters of the milling balls

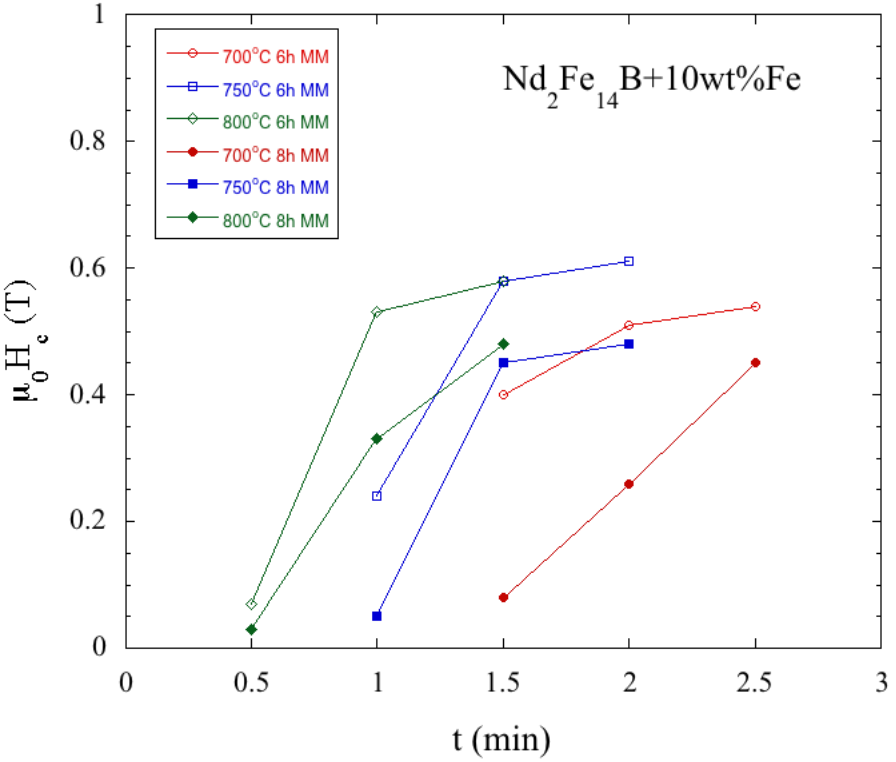
Different energy of milling

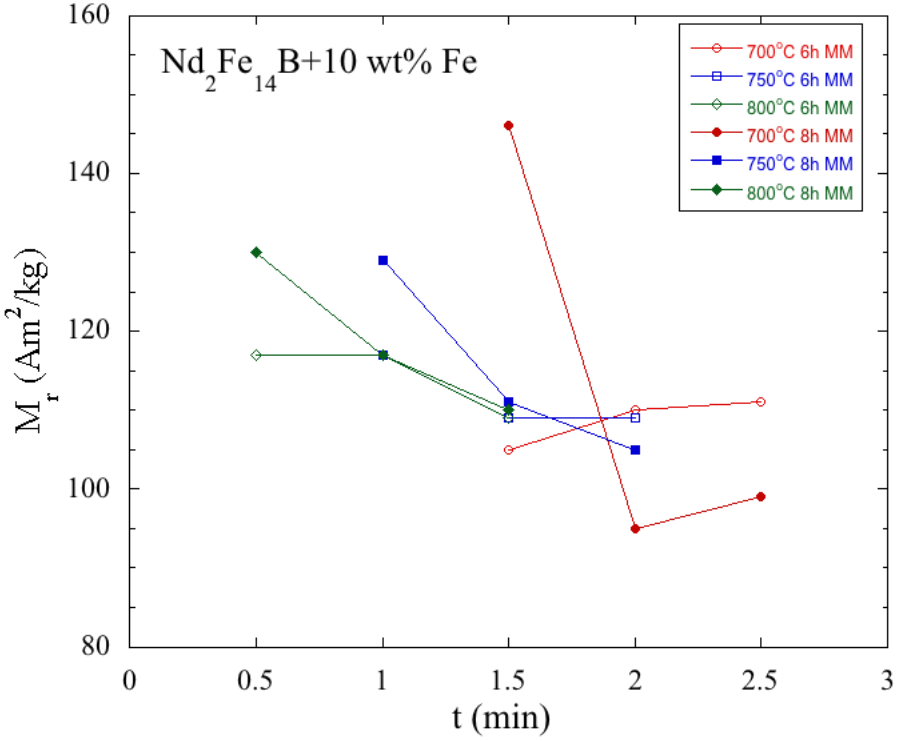
*The **filled** and **empty** symbols correspond to the samples milled with **Ø 10 mm** and **Ø 15 mm** balls respectively*

*The **better crystallinity of the hard** magnetic phase (for the less energetic MM) impose a **better coupling**.*

Milling time (h)	Annealing temperature (°C)	Annealing time (min)	*d* (nm)	$\mu_0 H_c$ (T)	M_r (Am²/kg)
6 (Ø 10 mm)	700	1.5	10	0.42	114
	750	2	15	0.44	114
		2	20	0.38	124
		2.5	21	0.41	117
	800	1.5	25	0.17	97
6 (Ø 15 mm)	700	2	17	0.48	114
	750	2.5	20	0.41	117
6	550 [10]	90	34	0.55	115
8 [7]	700	1.5	16	0.51	103
	800	1.5	26	0.54	96

Different times of milling = ***Different energy*** of milling





Lower milling energy

↓

Better $Nd_2Fe_{14}B$ ***crystallinity***

↓

Higher coercivity for the **6h MM** samples

Higher milling energy

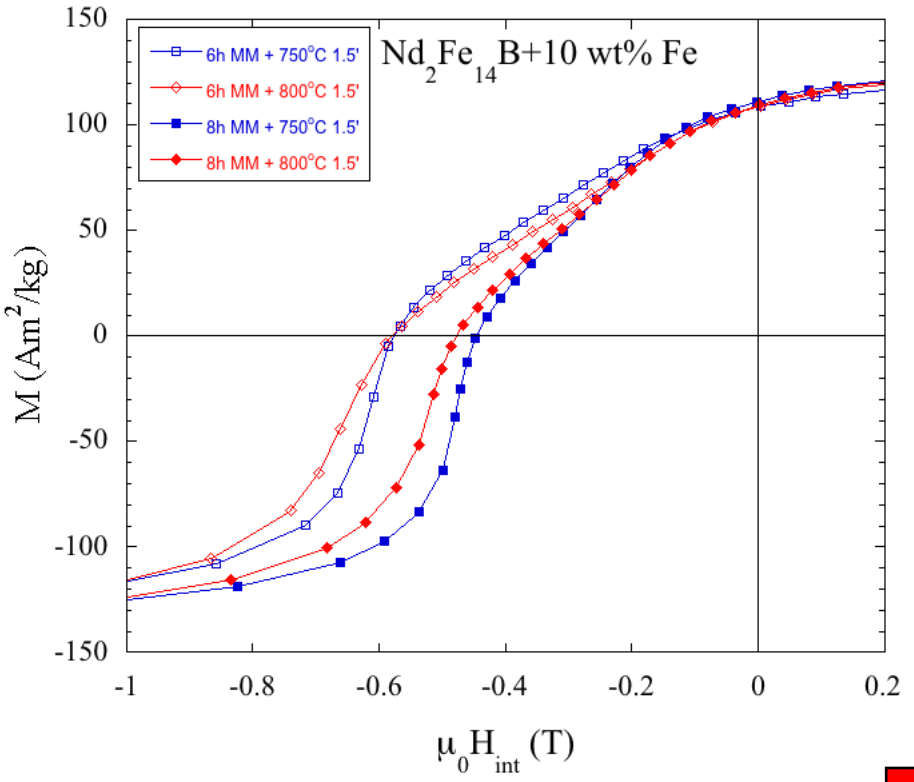
↓

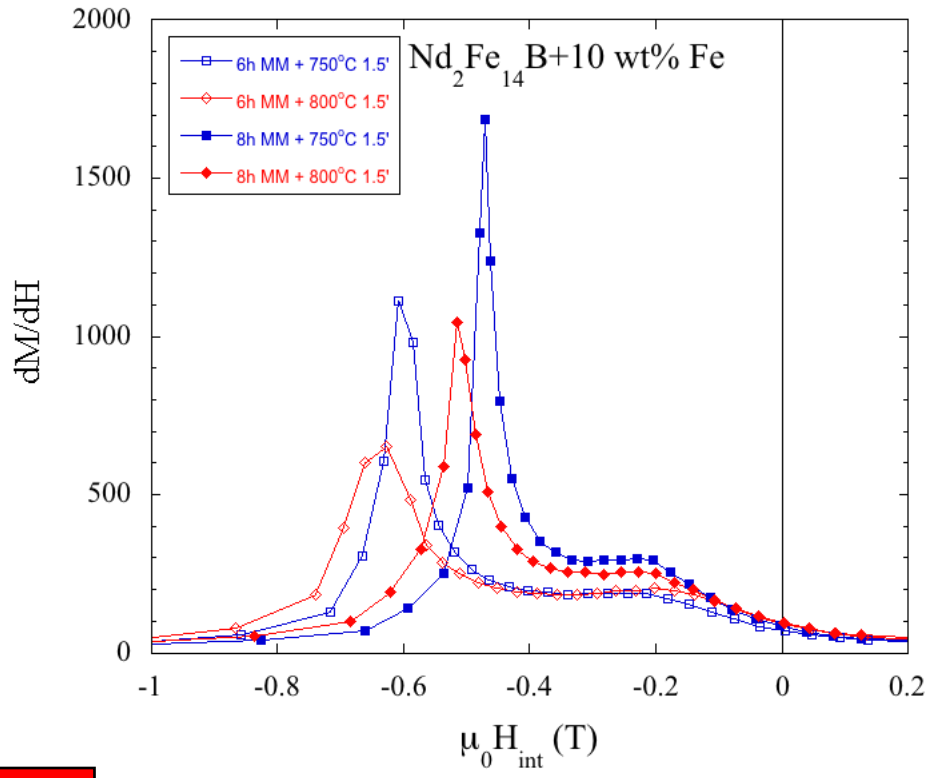
More Fe present due to $Nd_2Fe_{14}B$ decomposition during milling

↓

Slightly higher remanence for **8h MM**

Different times of milling = ***Different energy*** of milling





Best exchange coupling for **6h MM + 750° C**

Conclusions

- **The structure and microstructure have a strong influence on the hard/soft exchange coupling.**
- **The crystallinity and the anisotropy of hard magnetic phases are strongly influenced by milling.**
- **The characteristic diffractions peaks of hard magnetic phases are restored during heat treatment. The annealing induces also a refinement of the soft magnetic phase structure**
- **Lower milling energies increase the coercive field due to a reduced damaging of the hard phase crystal structure.**
- **Higher milling energies lead to a slight remanence increase due to a higher percentage of Fe present in the milled samples resulting from the $Nd_2Fe_{14}B$ decomposition during milling.**
- **The hard/soft interphase exchange coupling is more sensitive to the crystallinity of hard phase than to the small variations of the crystallite size of soft phase.**

Thank you for your attention

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PN-II-ID-PCE-2012-4-0470,
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