Propriétés magnétiques et structurales des nanocomposites magnétiques Nd2Fe14B/ α-Fe obtenus par broyage mécanique de haute énergie

Viorel POP, Sever Mican
Université Babeş-Bolyai, Faculté de Physique, 400084 Cluj-Napoca, Roumanie

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

Ionel CHICINAŞ
Département de Science et de Technologie des Matériaux, Université Technique de Cluj-Napoca, Roumanie

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Sommaire

- **Introduction**
- **Détails expérimentaux**
- **Structure et microstructure**
- **Couplage magnétique interphase**
- **Conclusions**

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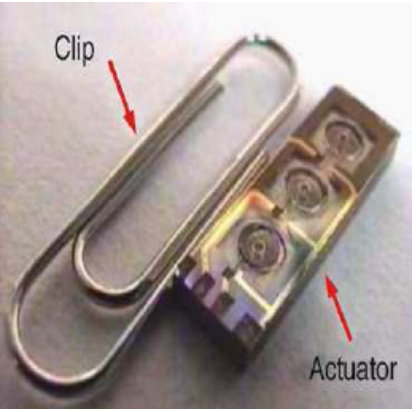
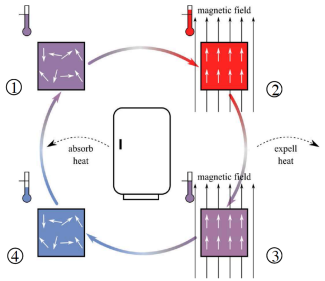


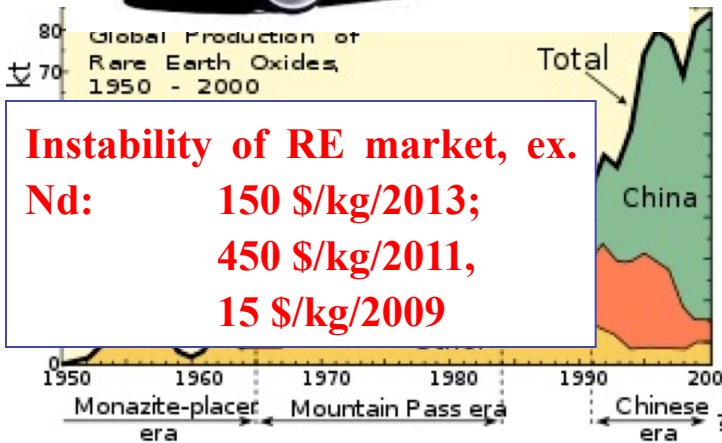


- magnetic materials are ***critical*** components in many devices and for advanced technologies.
- high performance magnet (HPM)/wind generator 1000-1600 kg/MW.
- motors and generators: **2 kg** HPM/hybrid electric vehicle-**20 million** vehicles by 2018.

HPM= **rare-earth** based magnets

China manages about 96 % of rare-earth resources in 2011

!!!



Instability of RE market, ex.

Nd: 150 $/kg/2013;
450 $/kg/2011,
15 $/kg/2009

Solutions ?

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Oui, nous devrons trouver des solutions !

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Oui, nous devrons trouver des solutions !

1. L'augmentation de l'efficacité d'utilisation.
2. Recyclage.
3. ***Nouvelles phases magnétiques*** sans-terre rare avec de propriétés magnétiques intéressantes pour les applications comme des aimants permanents et réfrigération magnétique: Fe-Co et Fe-Ni tétragonale, alliages Fe-Co ternaire ou quaternaire, $Fe_{16}N_2$, MnBi, MnAl, Mn_3Ga, alliages Heusler
4. Nanocomposites magnétiques dur/doux renforcés par l'échange ➔ ***Spring magnets***

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Solutions ?

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1. L'augmentation de l'efficacité d'utilisation.
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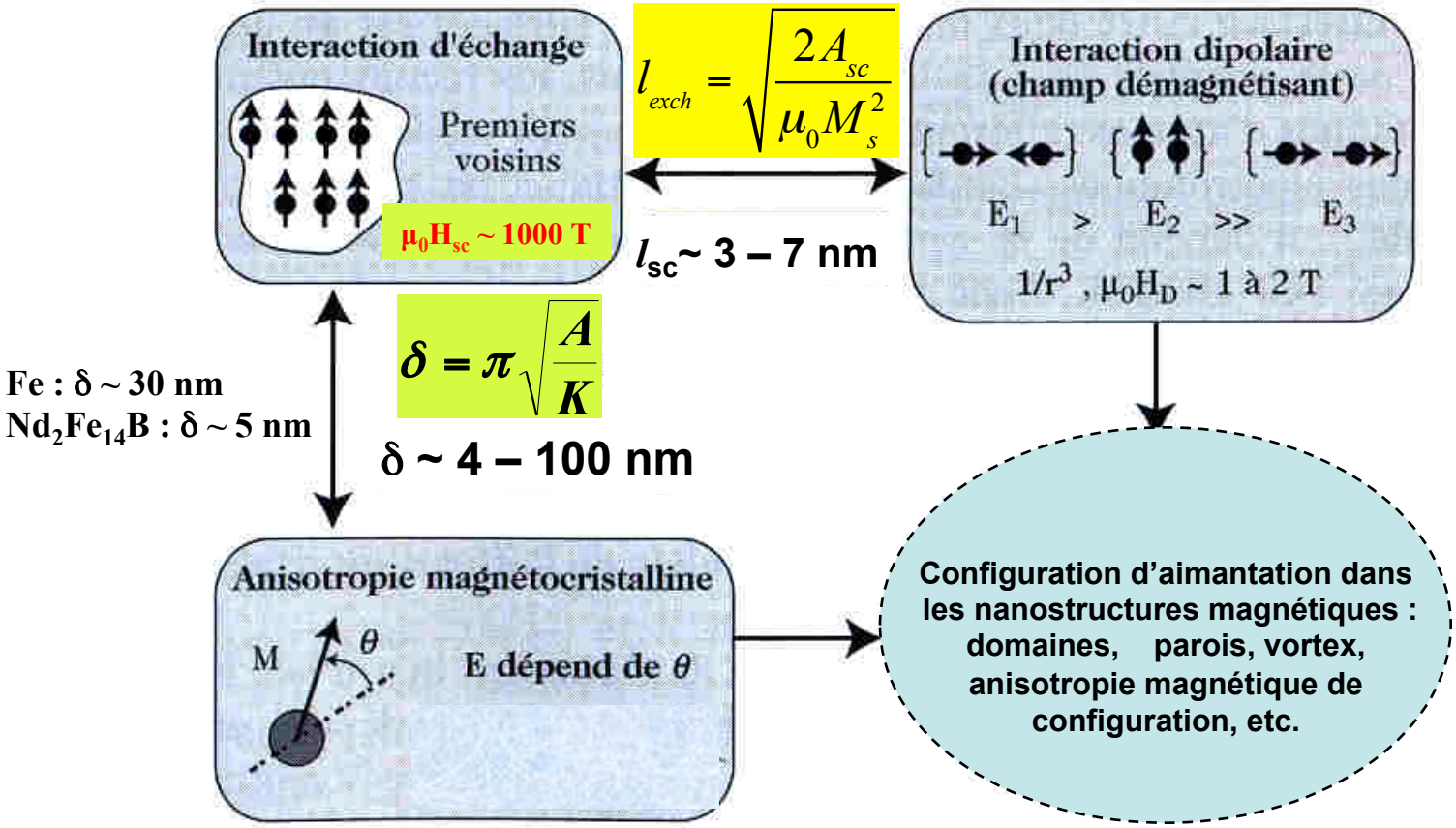
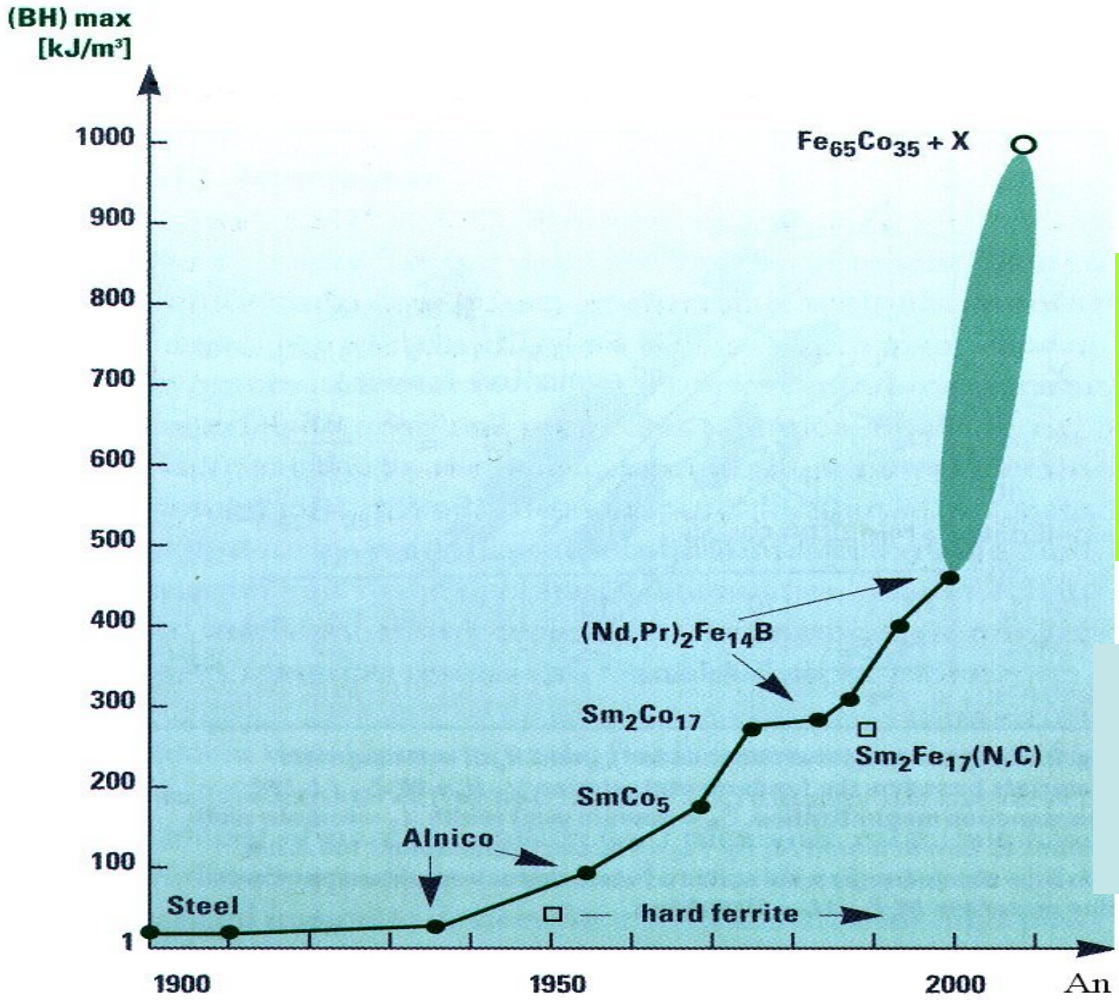
4. Nanocomposites magnétiques dur/doux renforcés par l'échange ➔ *Spring magnets*

Les nanomatériaux se comportent différemment de leurs équivalents microcristallins ou monocristaux parce que leurs dimensions caractéristiques sont plus petites que les longueurs caractéristiques de phénomènes physiques survenant dans les matériaux massifs.



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

Prédictions théoriques:



Meilleurs aimants permaments:
(BH)max ≈ 500 kJ/m3

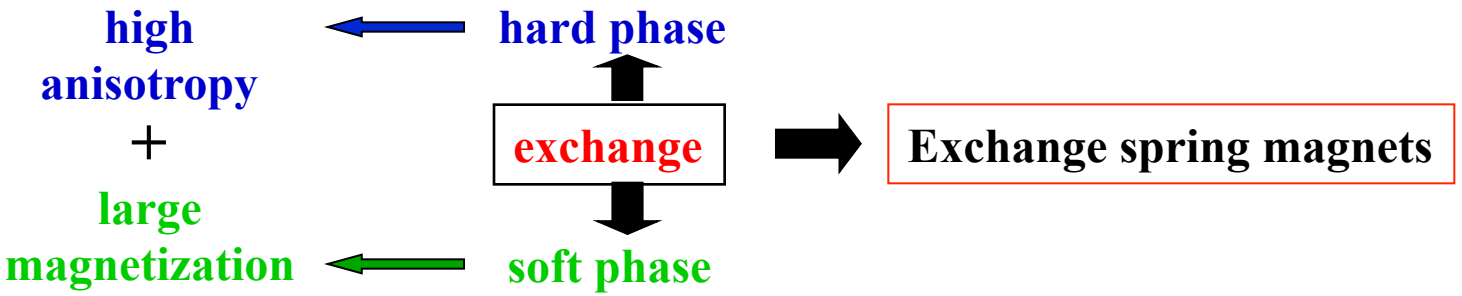
$(BH)_{max}$ = 1090 kJ/m³ pour nanostructures multicouches $Sm_2Fe_{17}N_3/Fe_{65}Co_{35}$

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

Les réalisations expérimentales: ??????????

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



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

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

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**

Nanocomposites preparés par broyage mécanique (MM)

- phases magnétiques durs $Nd_2Fe_{14}B$
- phases magnétiques douces α-Fe (10 wt%)

Differents paramètres de broyage:

1. Differentes billes: Φ 10 mm and 15 mm
2. Differente durée: 6 h and 8 h of MM

- Energie de broyage
- Traitement thermique

→ Taille des cristallites α-Fe

↔ Couplage d'échange interphase

→ Cristallinité de la phase dure

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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:

- Classical annealing: in vacuum/450-650 °C for 0.5 up to 10 h.
- Short time annealing: in argon/700, 750 or 800 °C for 0.5 to 3 min.

Eviter la diffusion interphase:

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

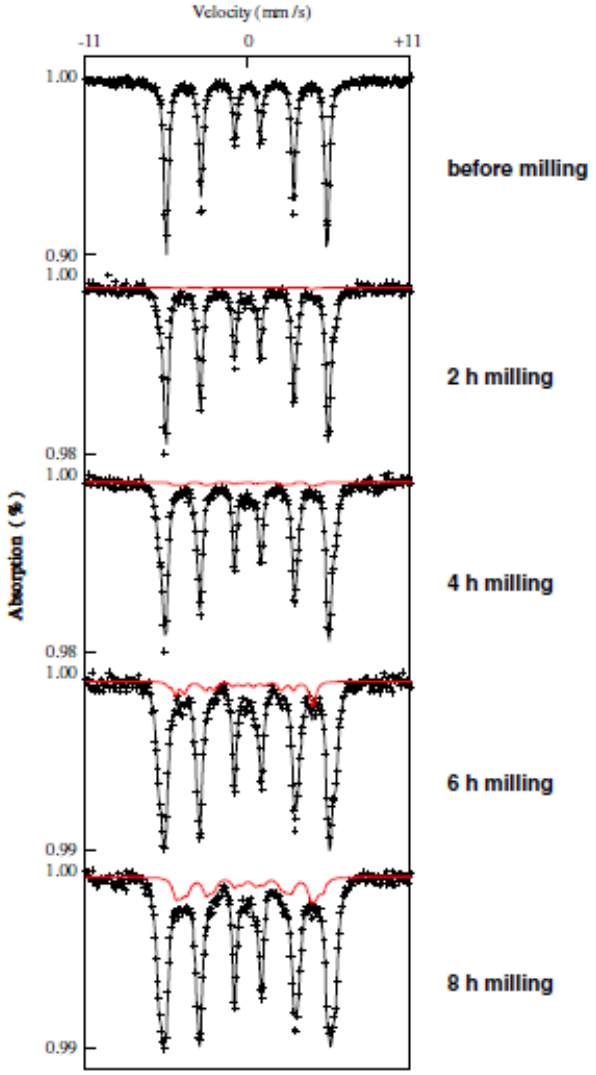


Figure 3. Room temperature Mössbauer spectra of the $SmCo_5$/Fe

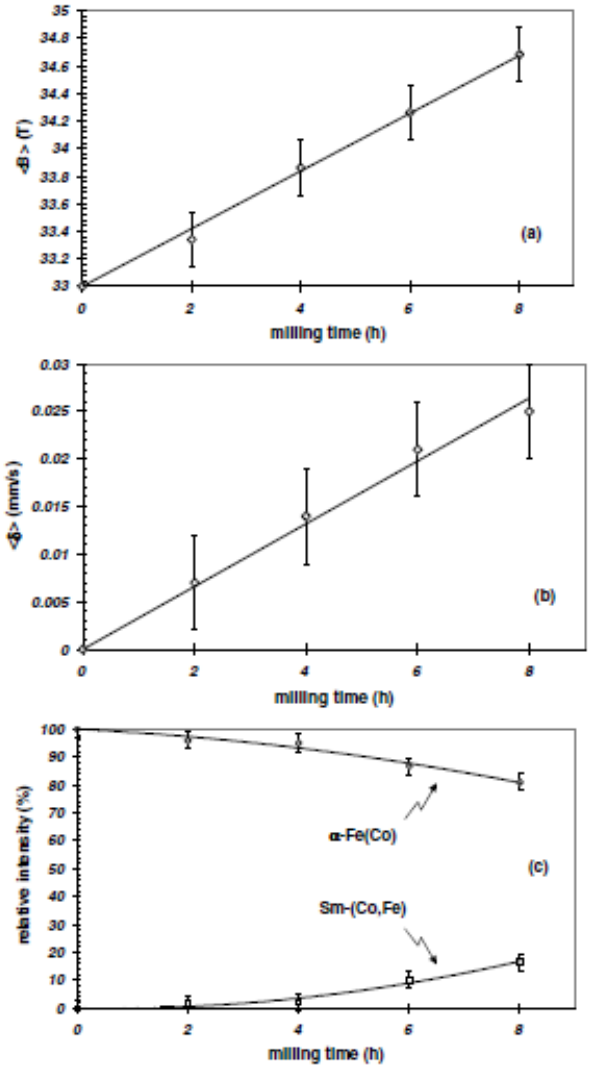
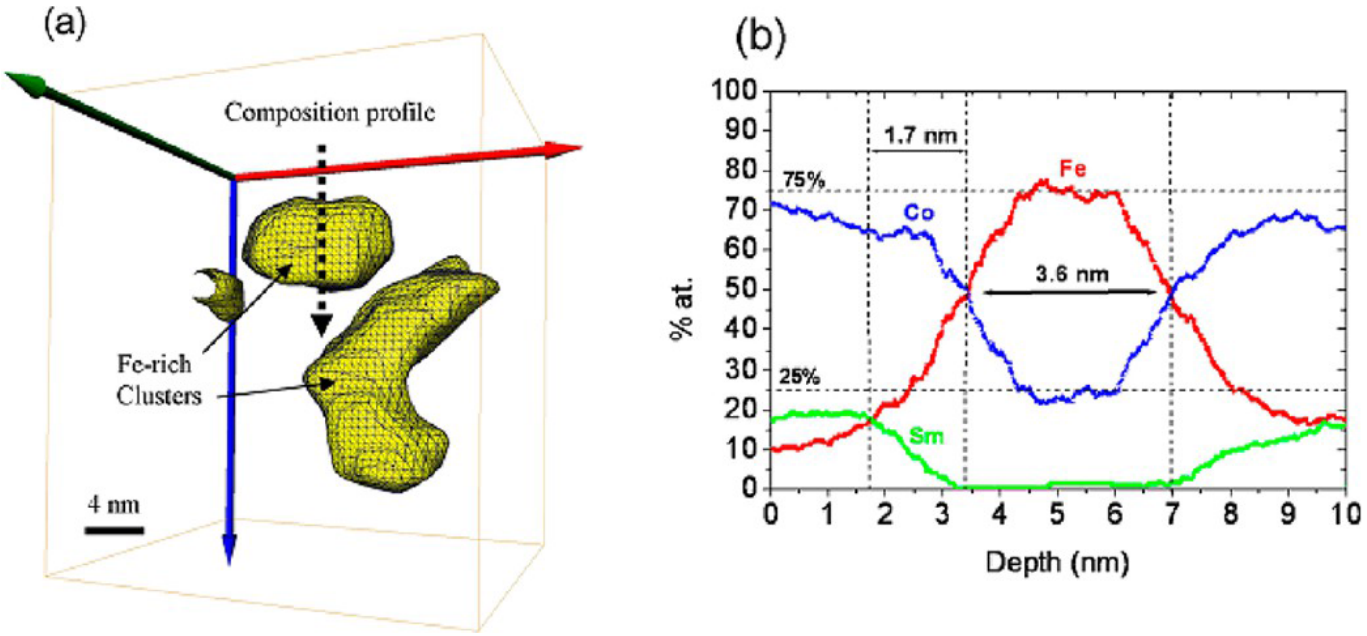


Figure 4. Evolution with the milling time of (*a*) the mean hyperfine

***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**

Eviter la diffusion interphase:

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**

Caractérisation des matériaux

- diffraction de rayons X (XRD)
- microscopie électronique
  - morphologie
  - composition de phase par EDX
- analyse thermique différentielle (DTA ou DSC)
- mesures magnétiques

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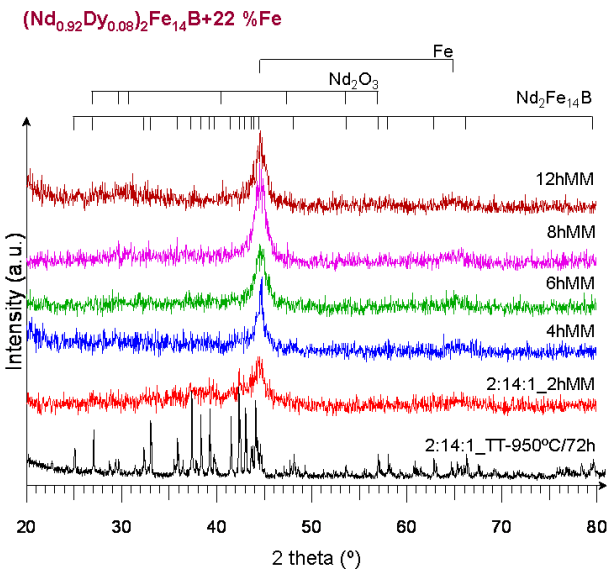
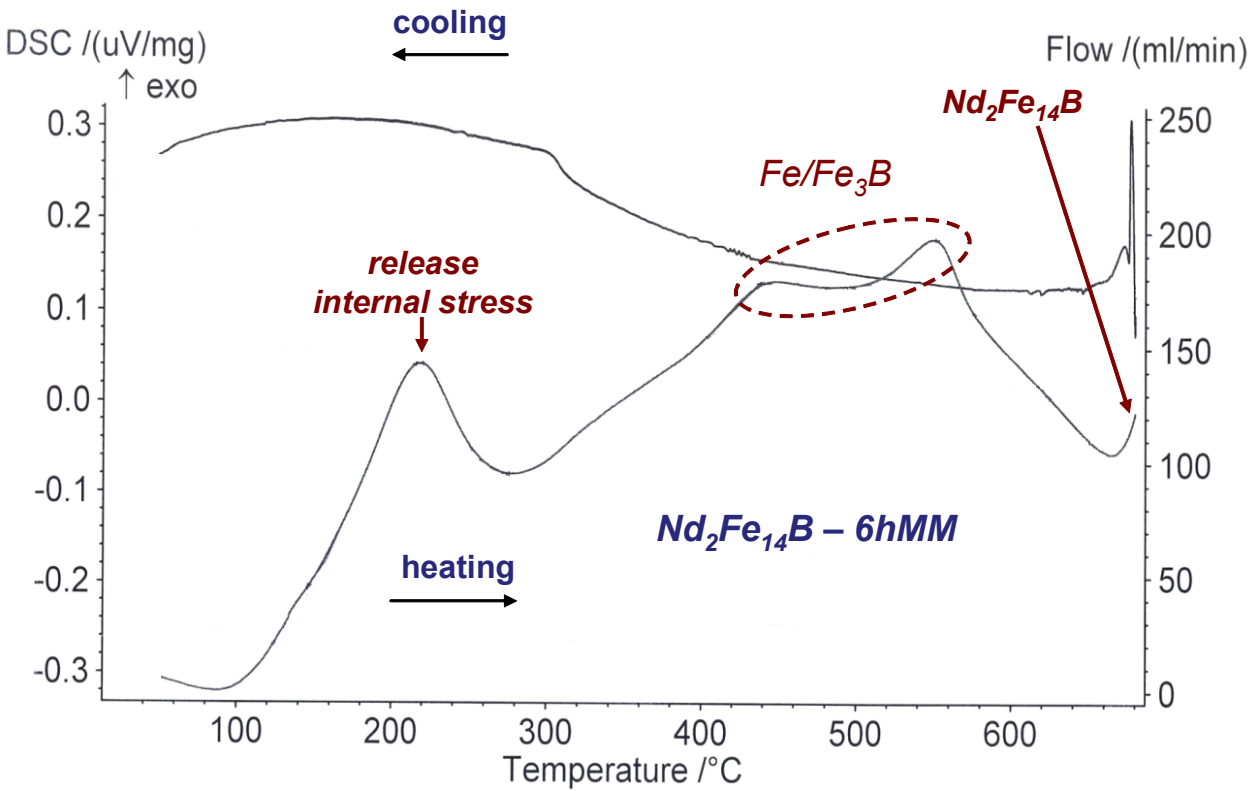
•The milled powders present poor crystallinity and a high defect density.

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

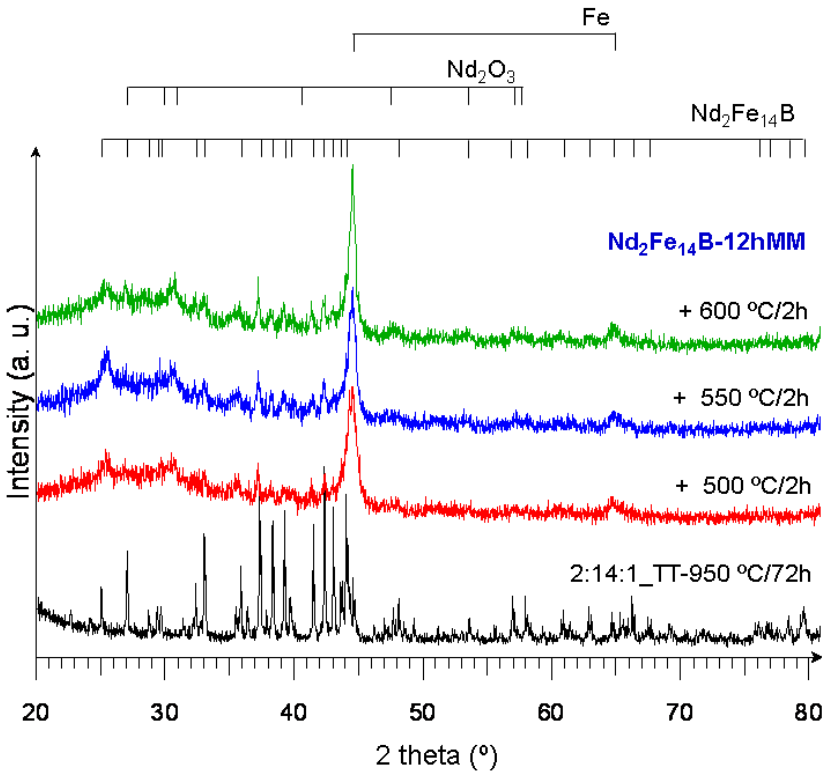
•By annealing we intended to recover the crystallinity of the hard phase and, in the same time, to hinder the growth of Fe crystallites during annealing.

•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 $Nd_2Fe_{14}B$/α-Fe magnetic composite.

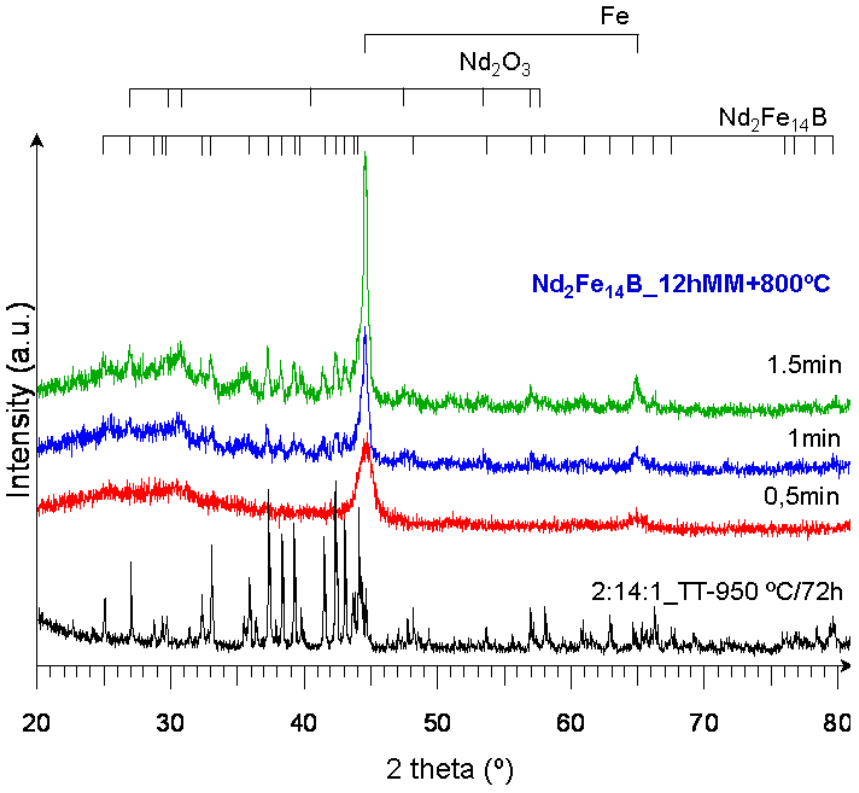




X-ray diffraction



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)

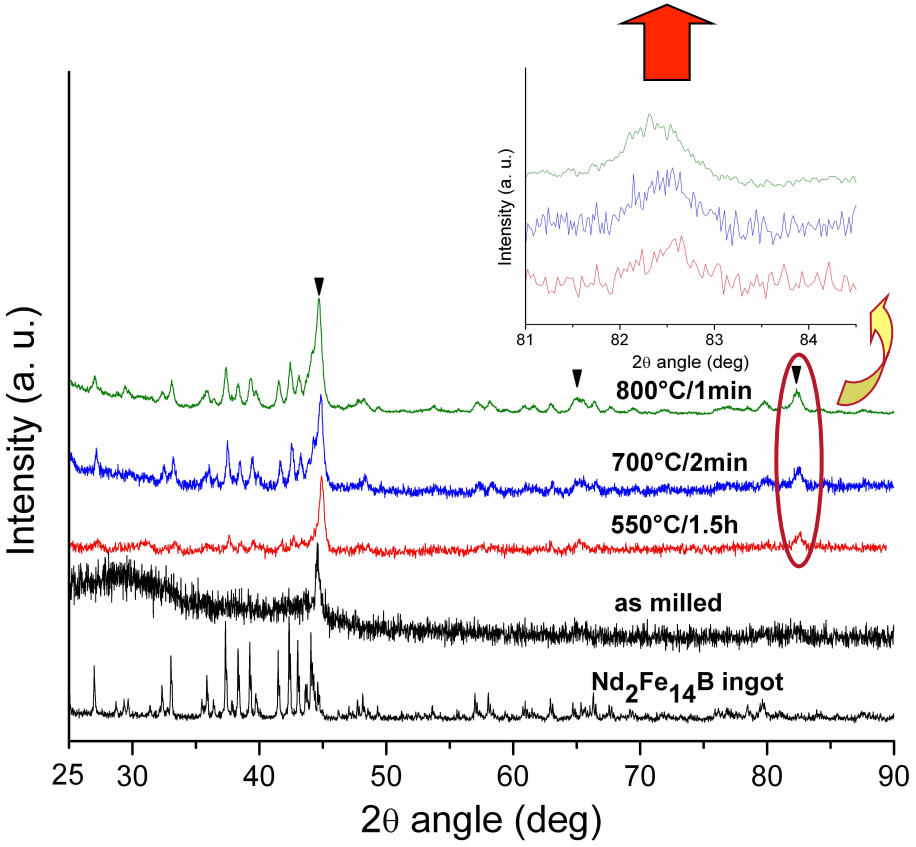
S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinas, V. Pop, J. Optoelectron. Adv. Mater. 12 (2010) 2126-2131

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

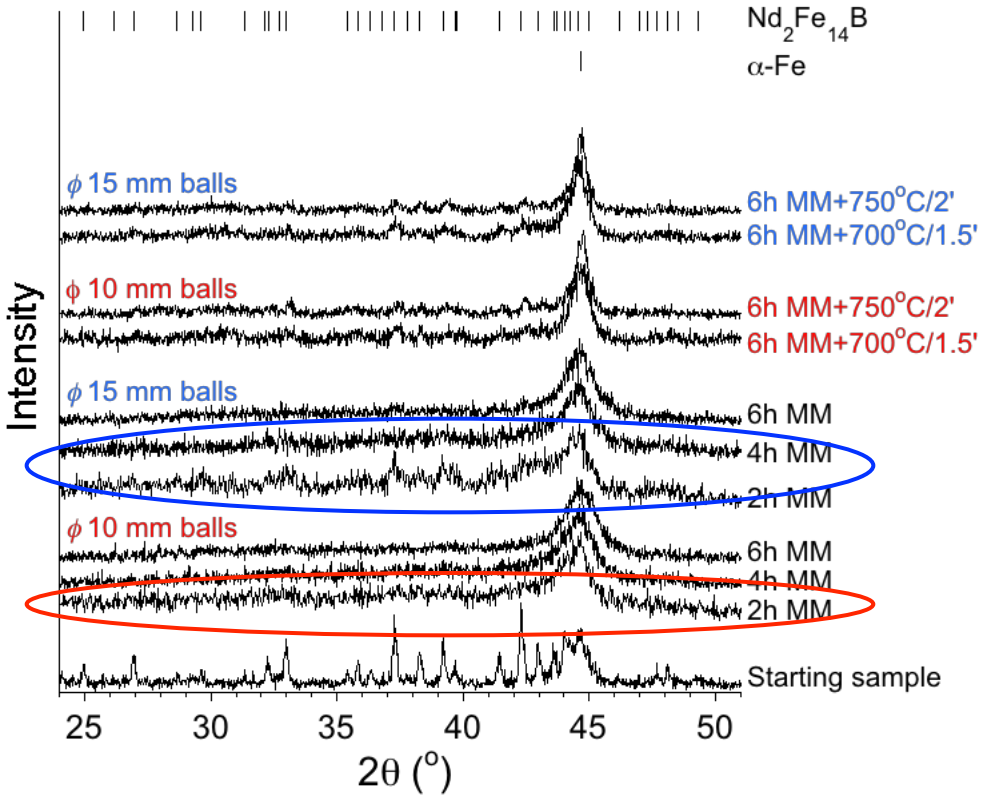
V. Pop et al, J. Alloys Compd. 581, 821-827 (2013).



$Nd_2Fe_{14}B$ + 10 % α-Fe

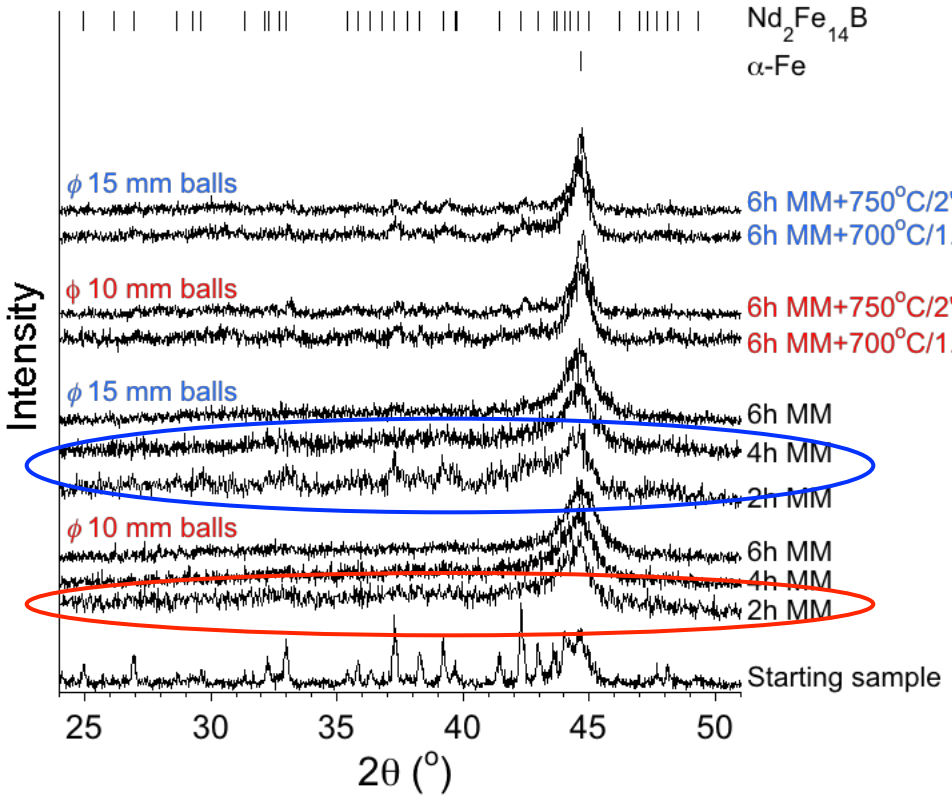
8h MM

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



Different diameters of the milling balls

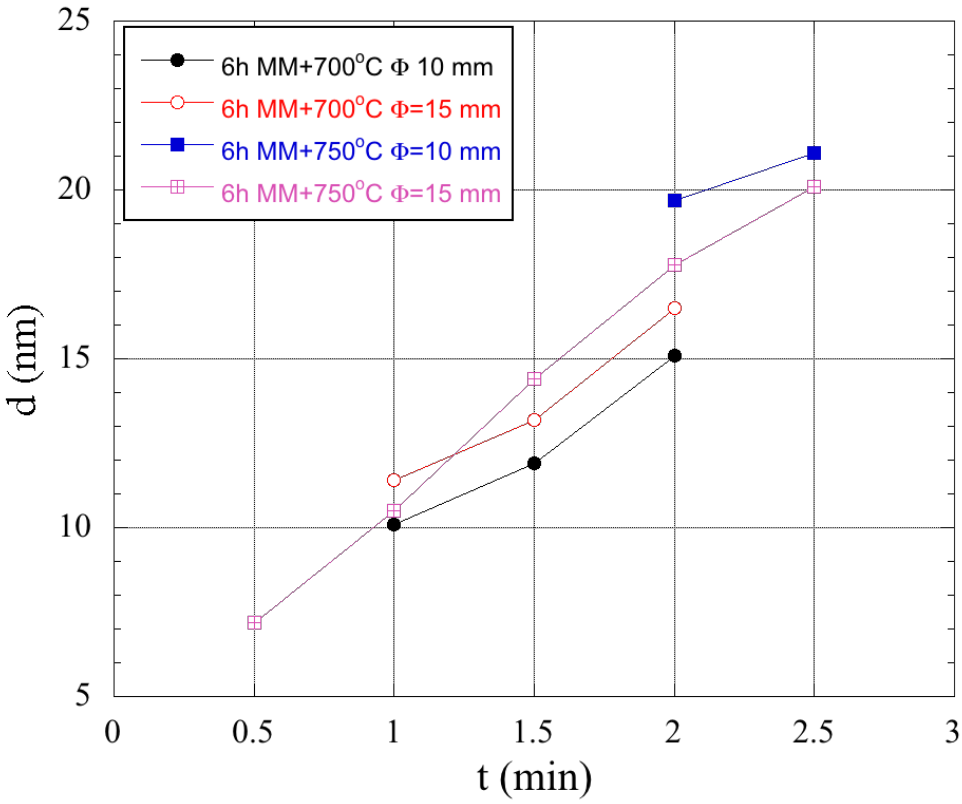
Different energy of milling



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

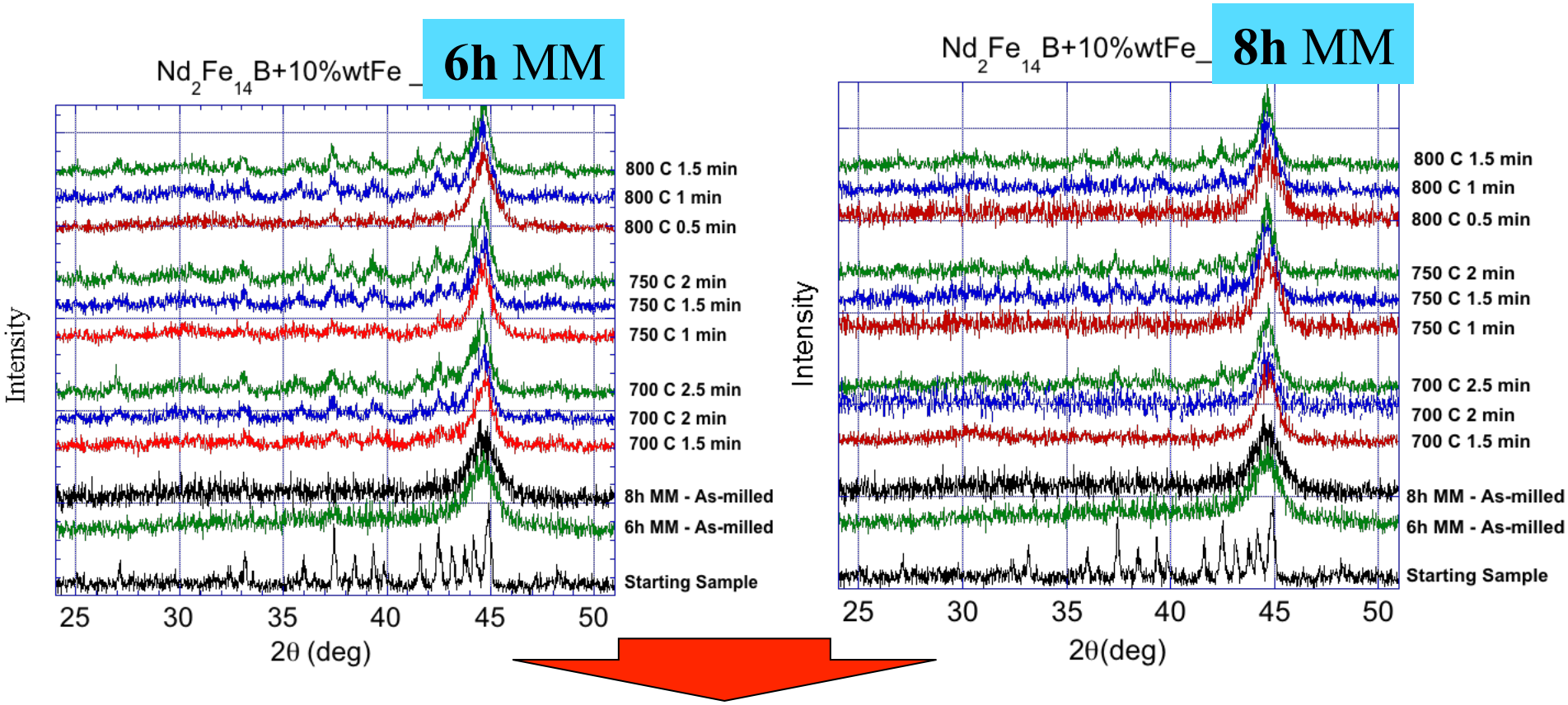


[7] V. Pop, S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinaş, *J. Alloys Compd.*, *509*, 2011, 9964.

[10] S. Gutoiu, E. Dorolti, O. Isnard, I. Chicinaş, V. Pop, *J. Optoelectron. Adv. Mater.*, *12*, 2010, 2126.

Different times of milling

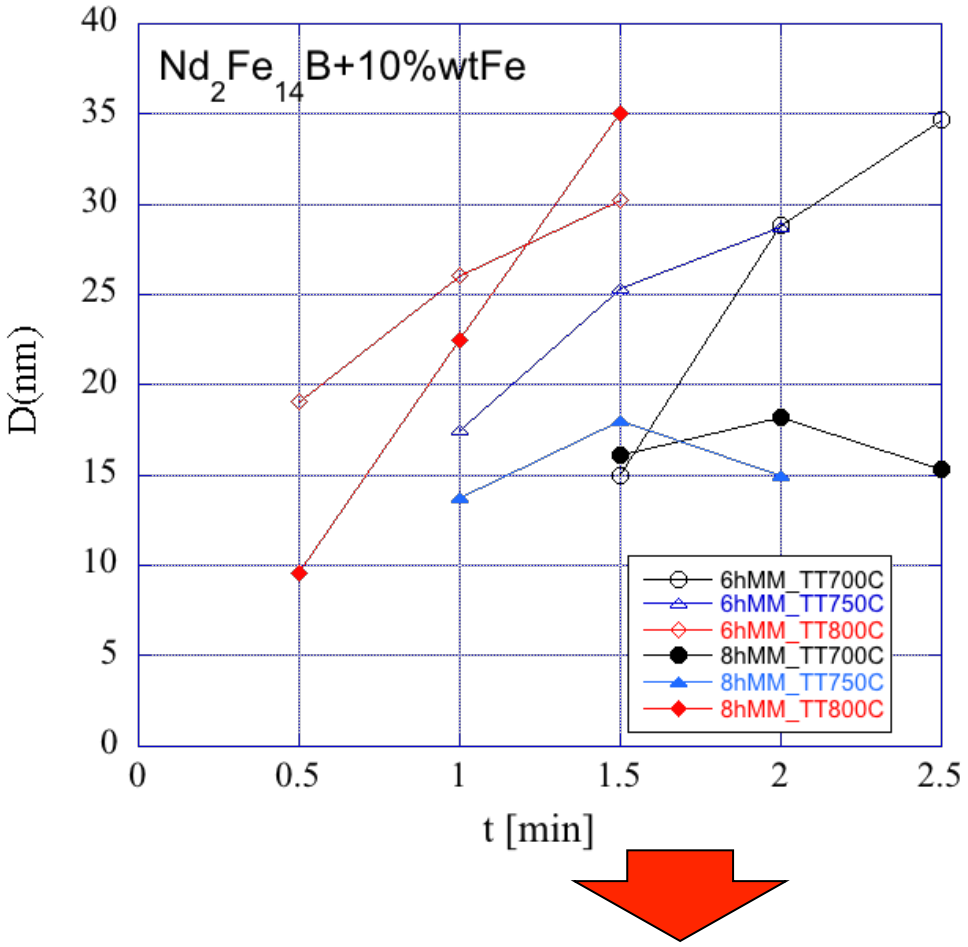
Different energy of milling



Better crystallinity for 6 h MM

Different times of milling

Different energy of milling



Smaller crystallites for 8 h MM

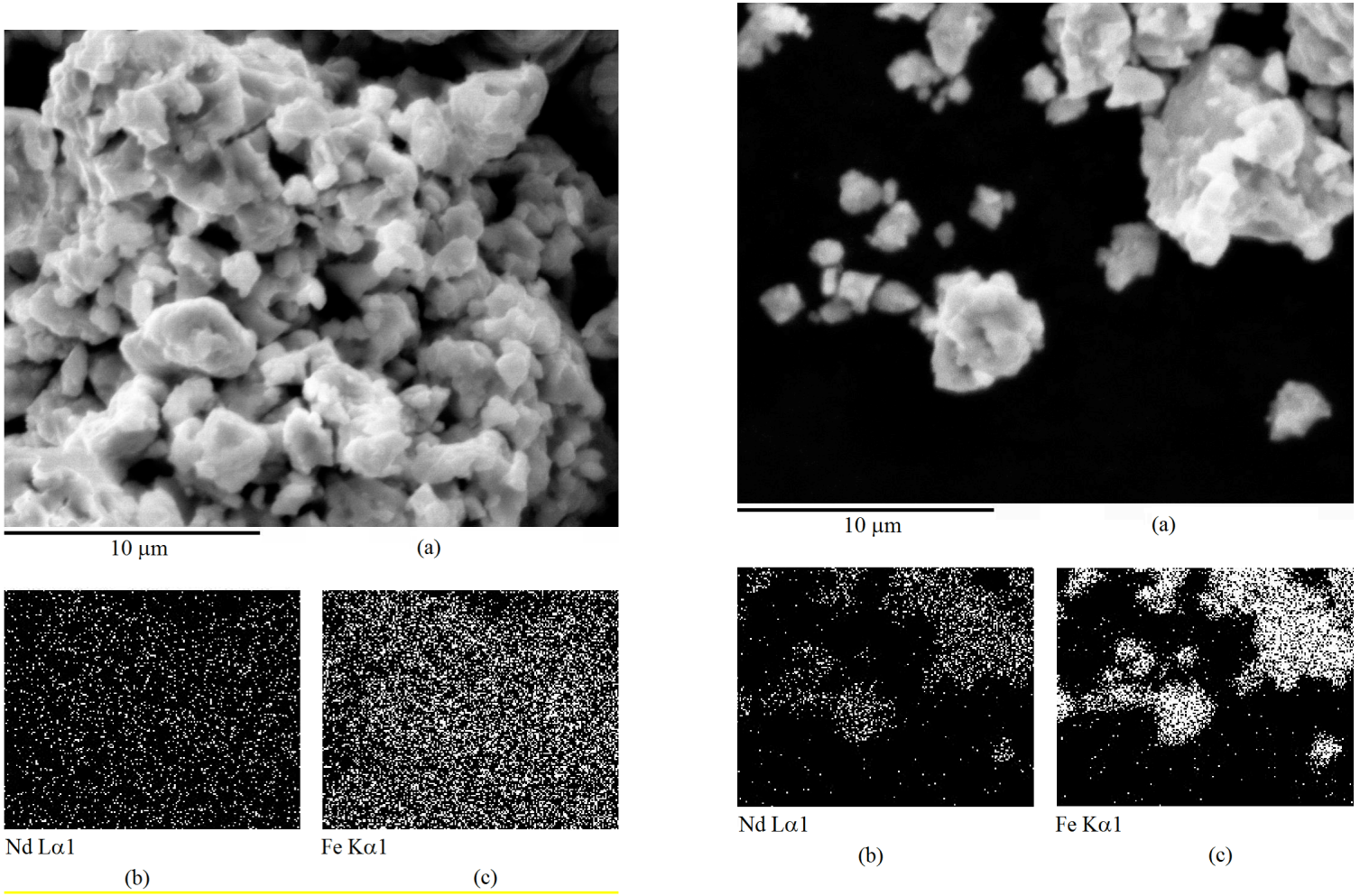


Fig. 3. SEM image (a) and EDX analysis of the same area for Nd (b) and Fe (c) for the 6h MM $Nd_2Fe_{14}B$+10 wt% α-Fe sample, annealed at 750 °C for 2 min.

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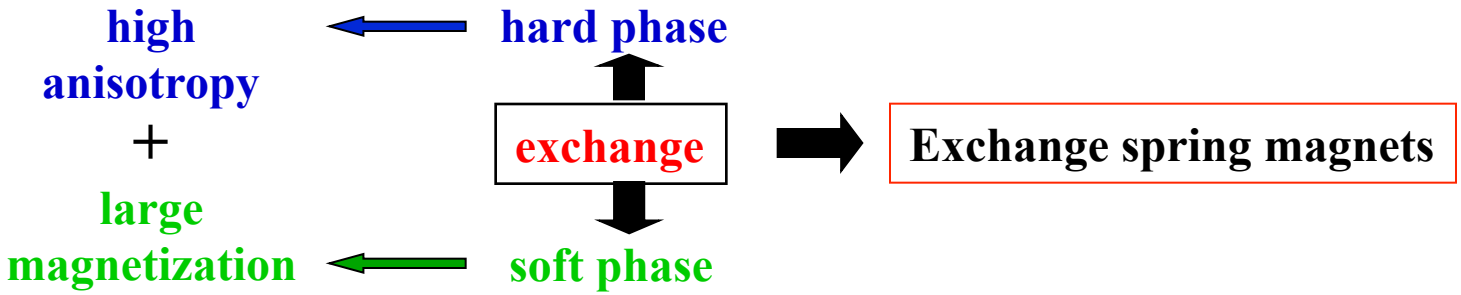
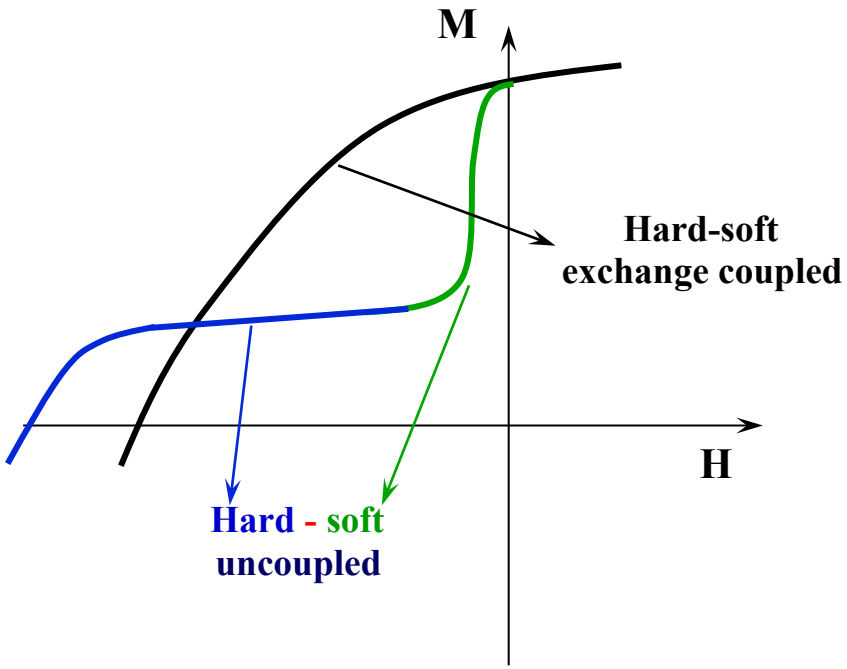
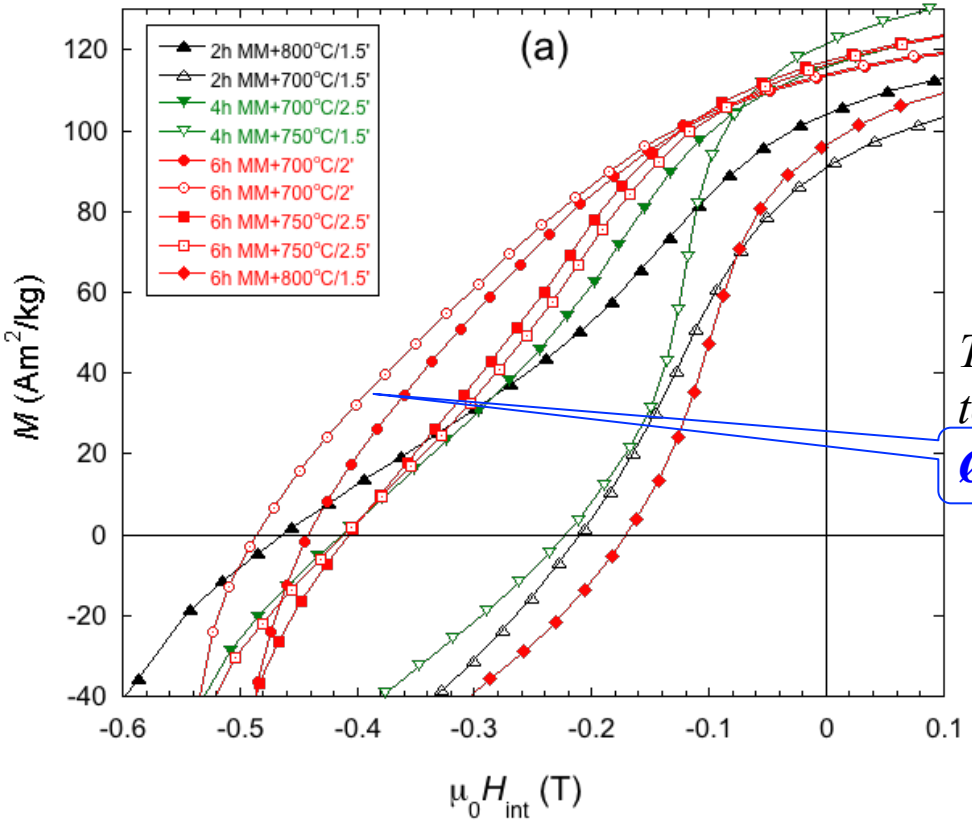

high
anisotropy
+
large
magnetization
hard phase
exchange
soft phase
Exchange spring magnets


M
H
Hard-soft
exchange coupled
Hard - soft
uncoupled



Different diameters of the milling balls

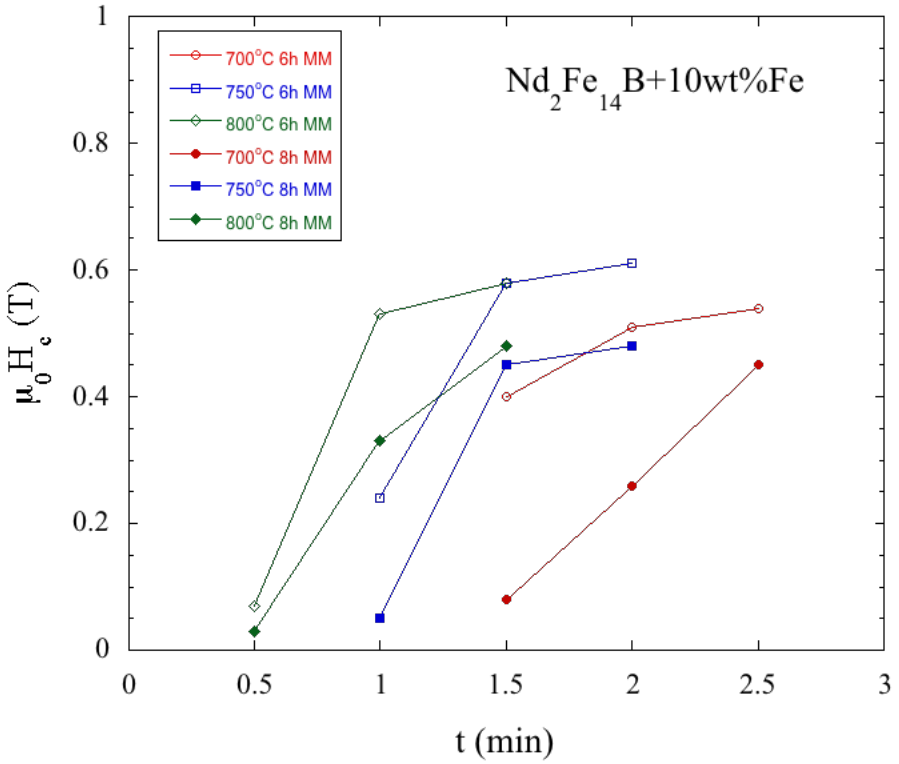
Different energy of milling

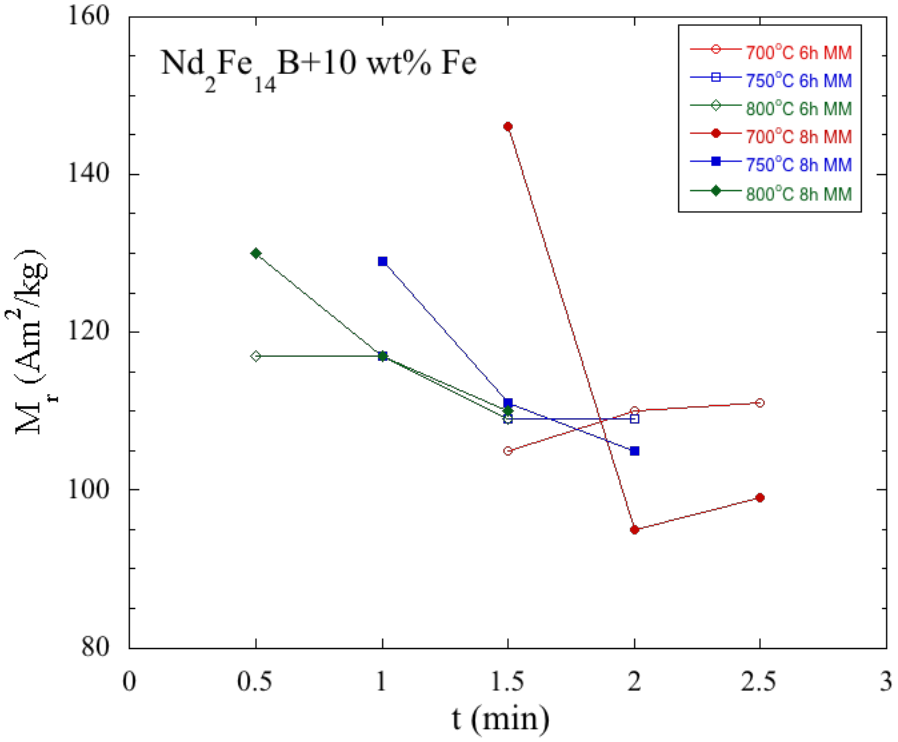
*The **filled** and **empty** symbols correspond to the samples milled with **Ø 10 mm** and **Ø 15 mm** balls respectively*

*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

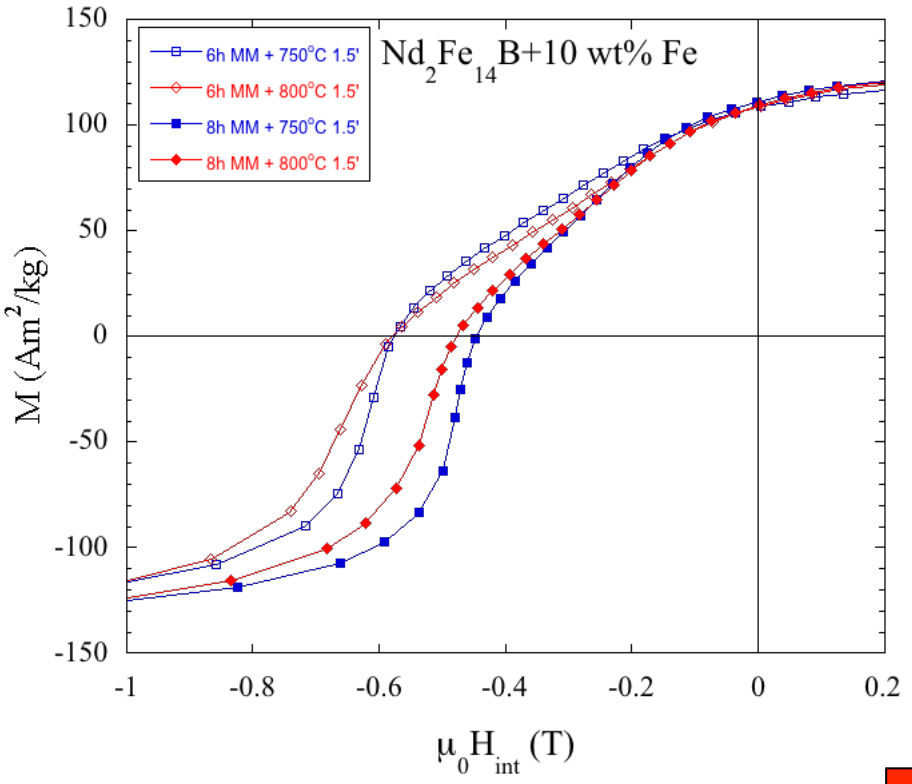
⇩

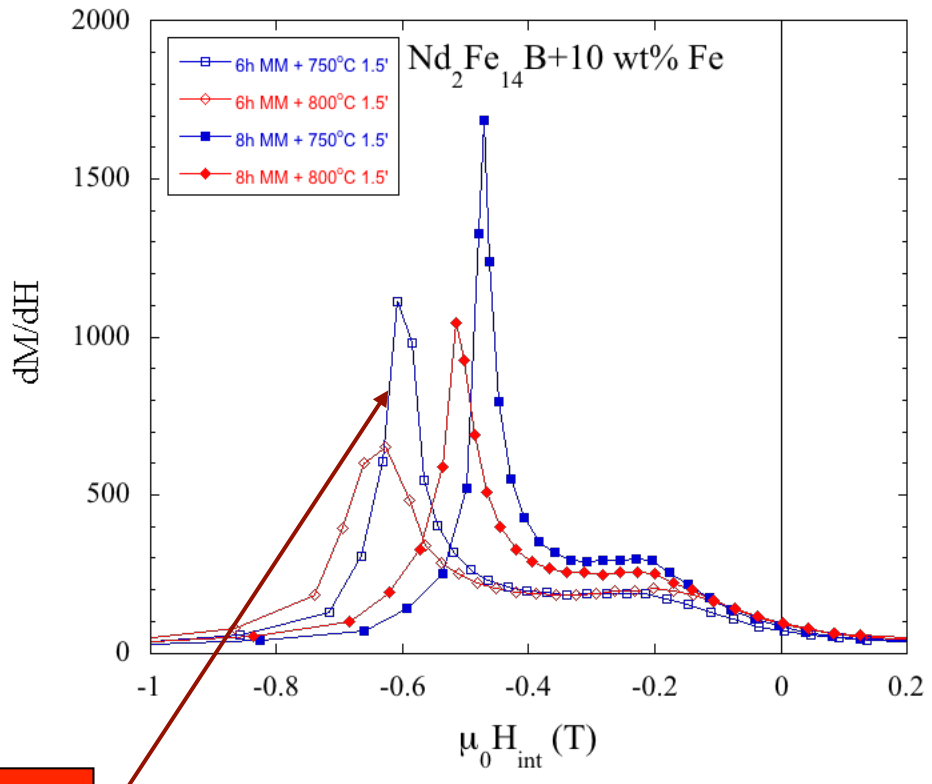
More Fe present due to $Nd_2Fe_{14}B$ decomposition during milling

⇩

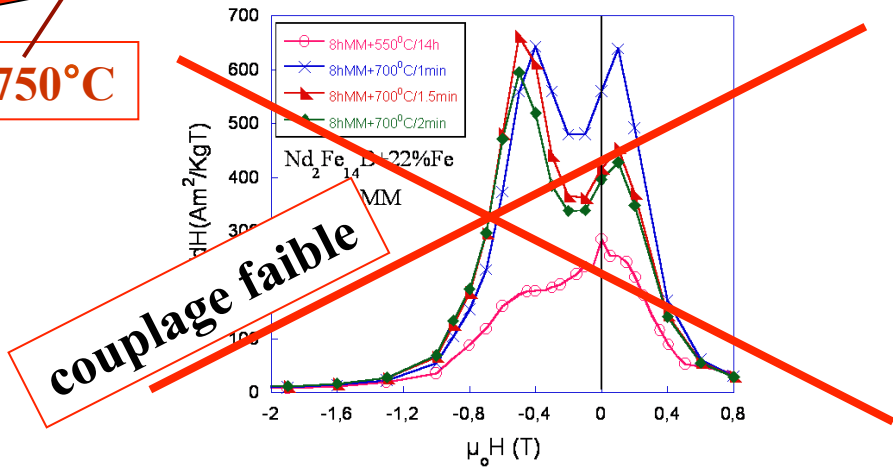
Slightly higher remanence for **8h MM**

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





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



couplage faible

Conclusions

- **La structure et la microstructure ont une forte influence sur le couplage d'échange doux/dur.**
- **La cristallinité et l'anisotropie des phases magnétiques dures sont fortement influencées par le broyage.**
- **Les pics caractéristiques de diffractions de la phase magnétiques dur sont rétabli après le traitement thermique.**
  Le recuit induit également l'affinement de la structure de la phase magnétique douce.
- **Une énergie inférieure de broyage augmente le champ coercitif grâce à une structure cristalline moins détruite.**
- **Une énergie supérieure de broyage conduit à une légère augmentation de la rémanence due à un pourcentage plus élevé de Fe présent dans les échantillons broyés issus de la décomposition $Nd_2Fe_{14}B$ lors du broyage.**
- **Le couplage d'échange doux/dur est plus sensible à la cristallinité de la phase dure que aux petites variations de la taille des cristallites de la phase douce.**

Merci pour votre attention

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