Nanocrystalline/nanostructured magnetic materials obtained by mechanical alloying/milling

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mechanical alloying: **powder alloying by high energy milling; it results new phases**

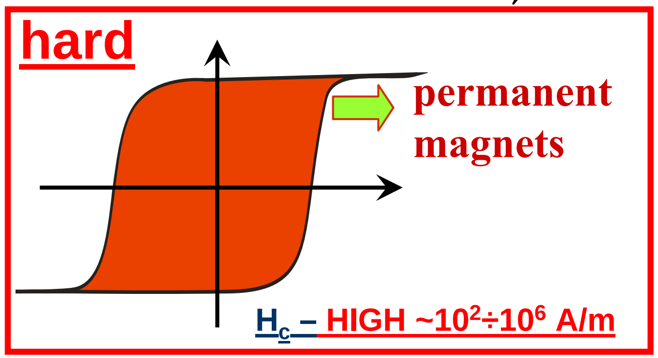
mechanical milling: **powder milling without producing chemical reactions; conservation of the initial phases.**

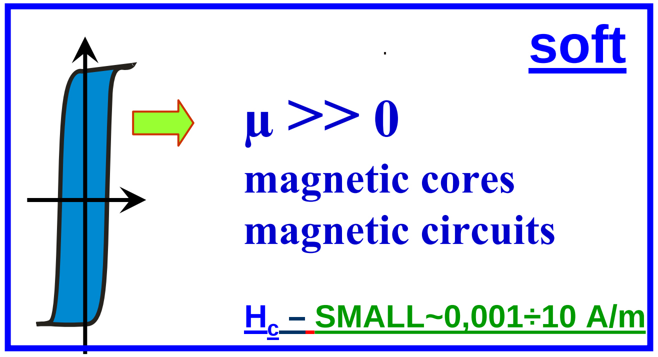
Nanocrystalline materials $(d < 100\ nm)$ obtained by:

- vapour - inert gas condensation, sputtering, plasma processing, vapour deposition
- liquid - electrodeposition, ***rapid solidification***
- solid - ***mechanical alloying***, severe plastic deformation, spark erosion

mechanical alloying, mechanical milling → → **nanostructured** **hard** / **soft** **and magnetic materials**

ANNEALING modifies the structure and microstructure





I. Hard Magnetic Nanostructured Materials:

hard/soft nanocomposite exchange spring magnets

- Babes-Bolyai University Cluj Napoca

Viorel Pop

II. Soft Magnetic Nanocrystalline Materials

- Technical University of Cluj-Napoca, Romania

Ionel Chicinaş

National partners

in research projects as RELANSIN, MATNANTECH, CERES, from PNCDI II, etc

Partners: INCDFM Bucharest (M. Valeanu), ICPE-CA Bucharest (W. Kappel), INCDTIM Cluj (O. Pana), Univ. Al. I. Cuza Iasi (A. Stancu), INCDFT-IFT Iasi (H. Chiriac).

European partners

Néel Institute and University Joseph Fourier Grenoble, University of Rouen, University of Nantes, Chemnitz University, CNRS Toulouse

5 PhD thesis connected to these subjects

Material preparation

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

Starting materials:

- **hard magnetic phases :**
  $SmCo_5$, $SmCo_3Cu_2$, $R_2Fe_{14}B$
  ingots – prepared by melting

- **Soft magnetic phases:**
  Fe NC 100.24 powder (Höganäs), (< 40 µm), 123-carbonil nickel (5-7 µm),
  NC 100.24 (Hoganas) Fe powders, (< 40 µm) Mo powder (Sinterom SA) (<10 µm),
  Cu powder (Tehnomag SA)

Mechanical milling

- **in Ar atmosphere for 1.5 – 52 h**

Annealing:

- **in vacuum/450-800 °C for 5 min. up to 10 hours**

Material characterisation

- X-rays diffraction (XRD)
- Electron microscopy (SEM and TEM)
  - morphology
  - chemical composition checked by EDX
- DTA, DSC
- Magnetic measurements
- Mössbauer spectrometry

I. Hard Magnetic Nanostructured Materials: hard/soft nanocomposite exchange spring magnets

high anisotropy ← hard phase

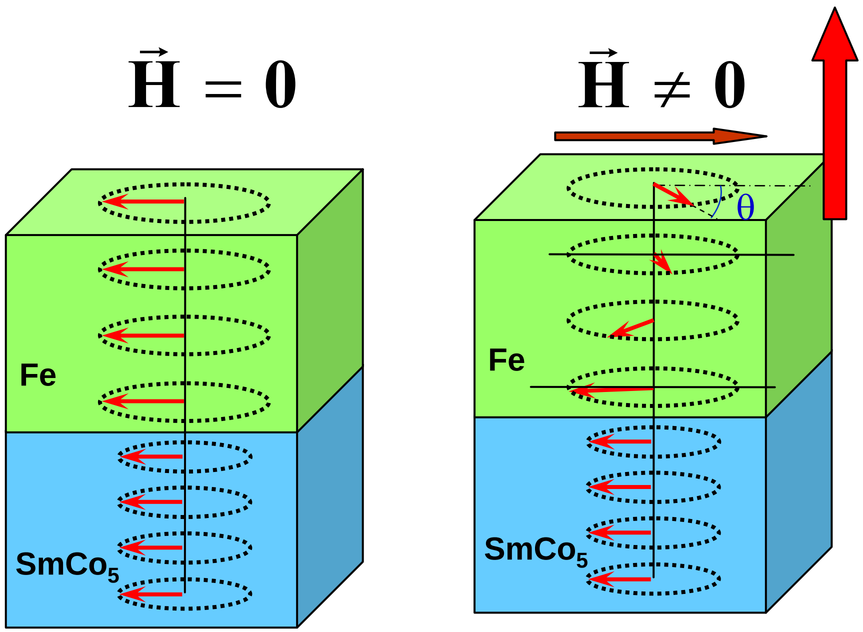
exchange → Exchange spring magnets

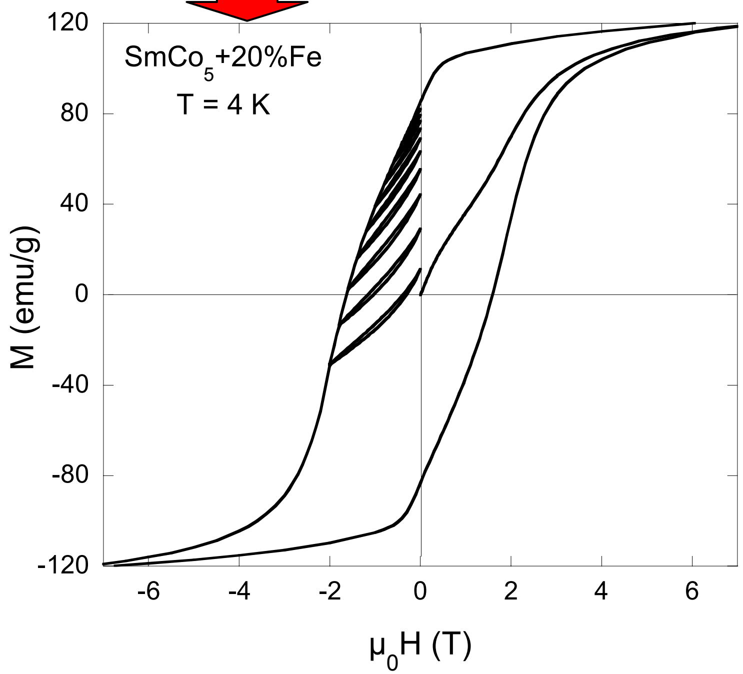
\+ large magnetization ← soft phase

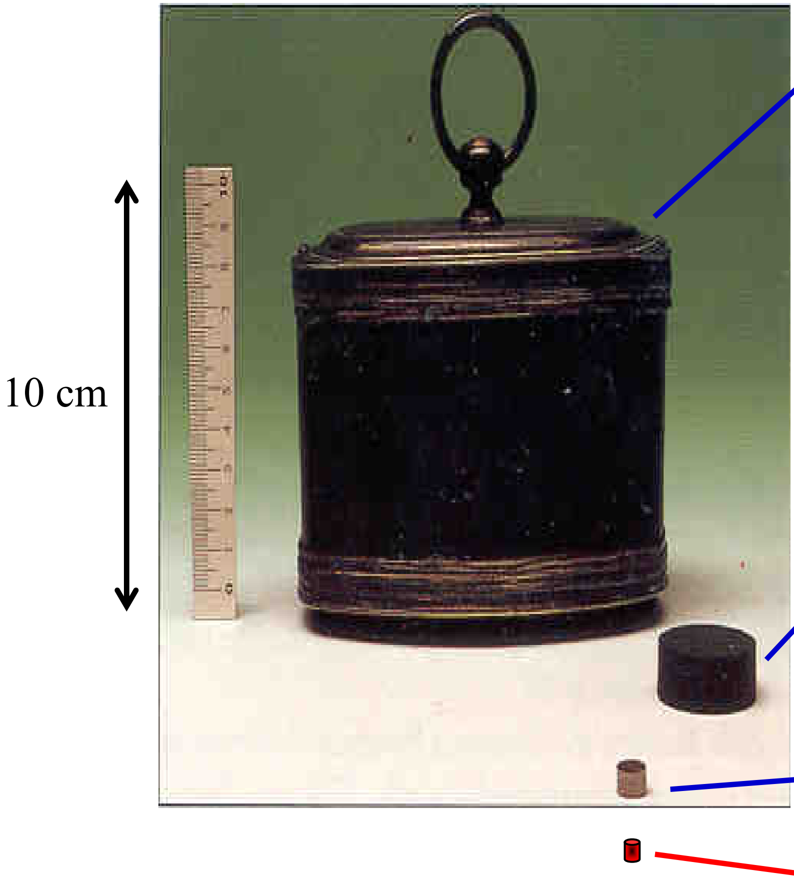
Large reversible demagnetization curve

+

Enhanced remanence $m_r > 0.5$ ($mr = M_r/M_s$)







a magnetit magnet (1750)

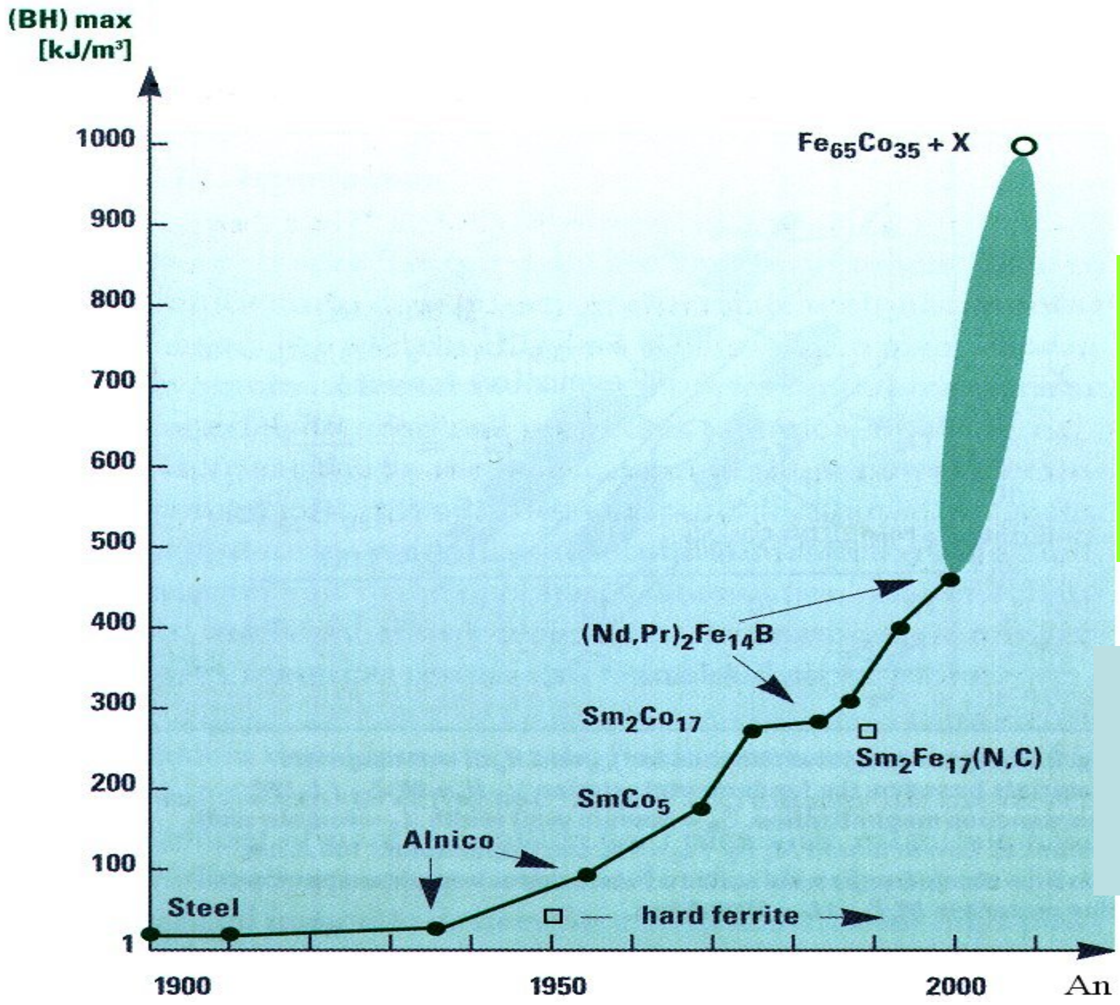
A ferrite magnet (1940)

rare earth based magnet
(1980)

exchange-spring magnets
(2???)

All this magnets have the same energy !

Theoretical predictions:



Best magnets on the market: (*BH*)max ≈ 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

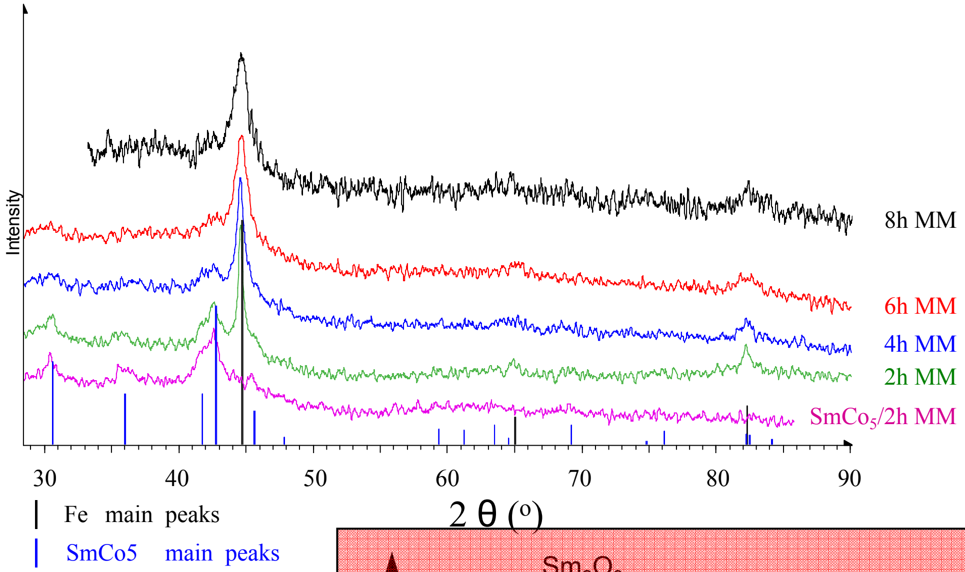
Experimental realisations: ??????????

Inter-phase Exchange coupling

Hard/Soft nanocomposites magnetic materials

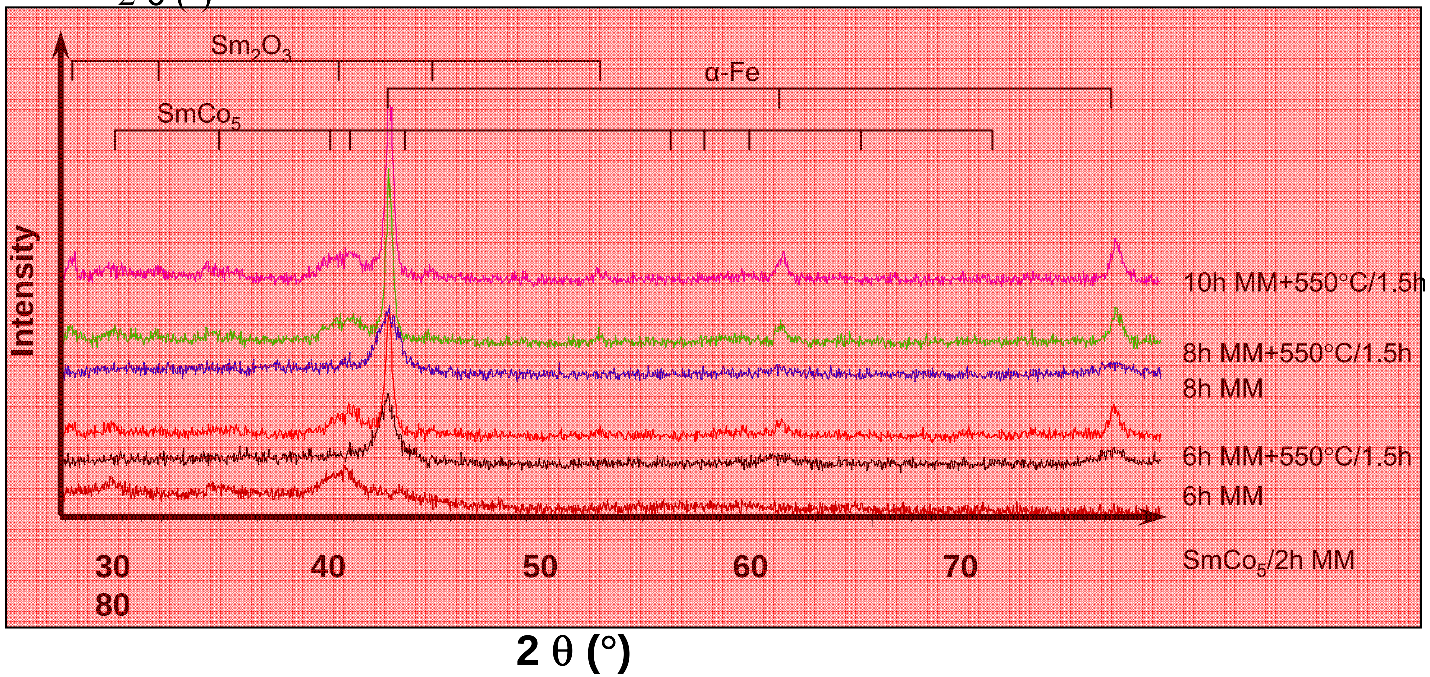
$SmCo_5$ + α-Fe	***Mechanical milling***
$SmCo_3Cu_2$ + α-Fe	+
$R_2Fe_{14}B$ + α-Fe	***annealing***

$SmCo_5$+20 wt% Fe



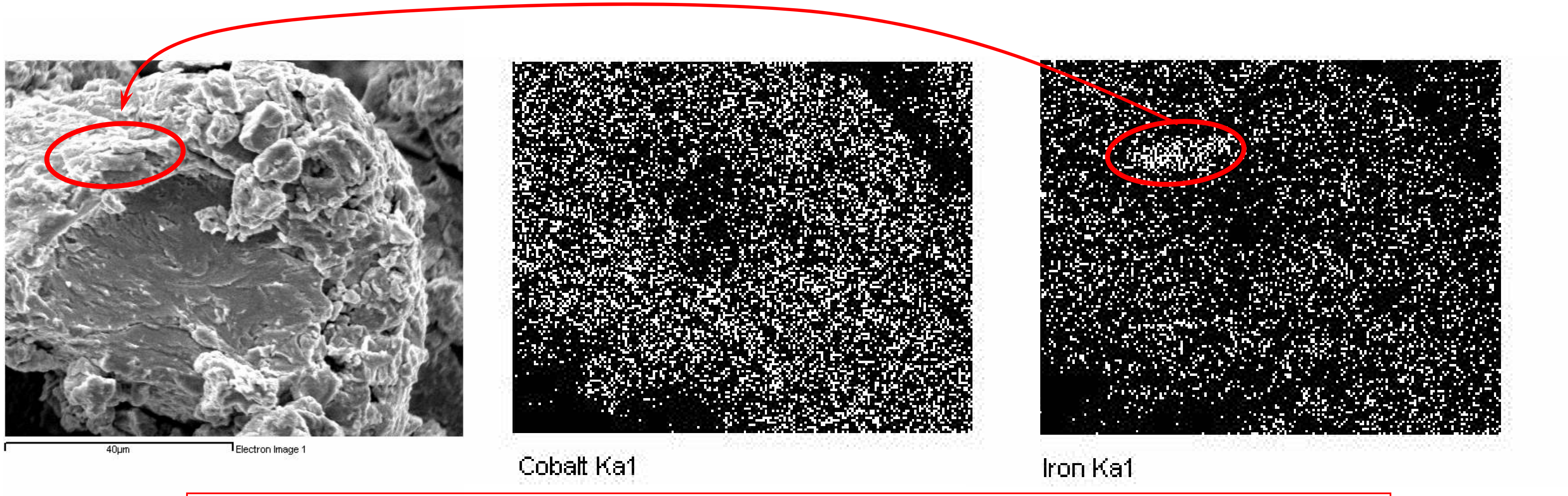
As milled samples

Annealed samples

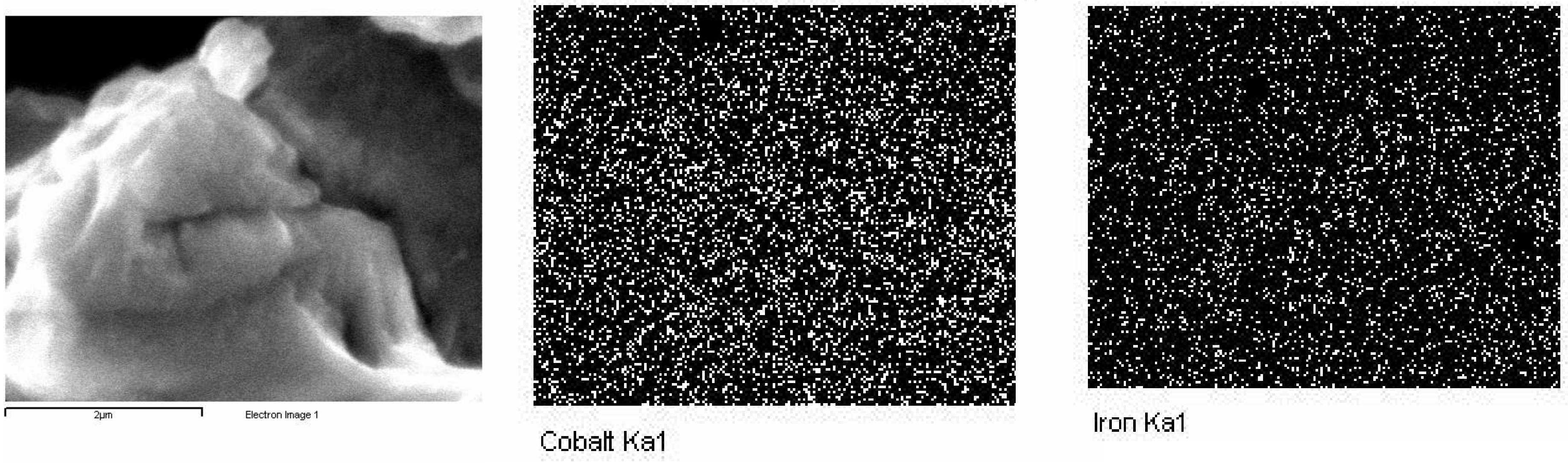


V. Pop, O. Isnard, I. Chicinas, D. Givord, J.M. Le Breton, J. of Optoelectron. Adv. Mater. 8 (2006) 494.

D. Givord, O. Isnard, V. Pop, I. Chicinas, J. Magn. Magn. Mater. 316 (2007) e503–e506



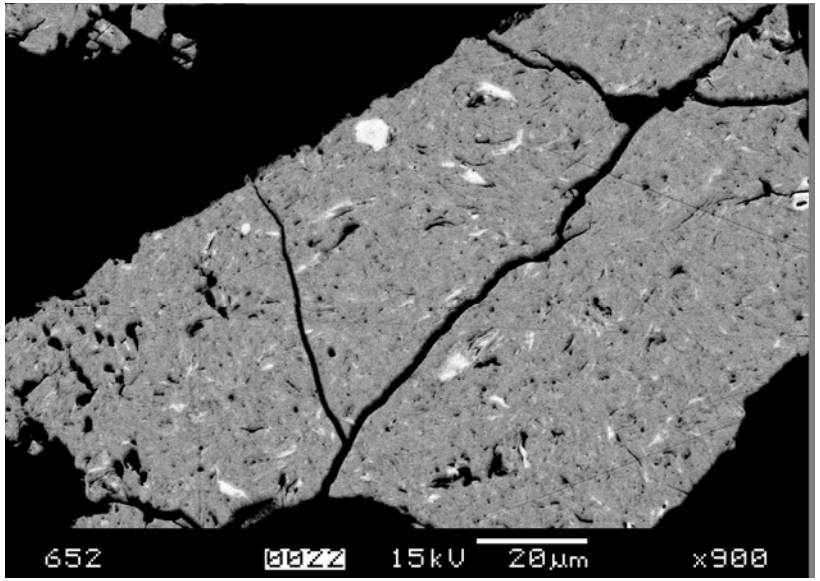
SEM – EDX → composition homogeneity of SmCo5 +20% Fe 2h MM



SEM – EDX → composition homogeneity of SmCo5 +20% Fe 8h MM

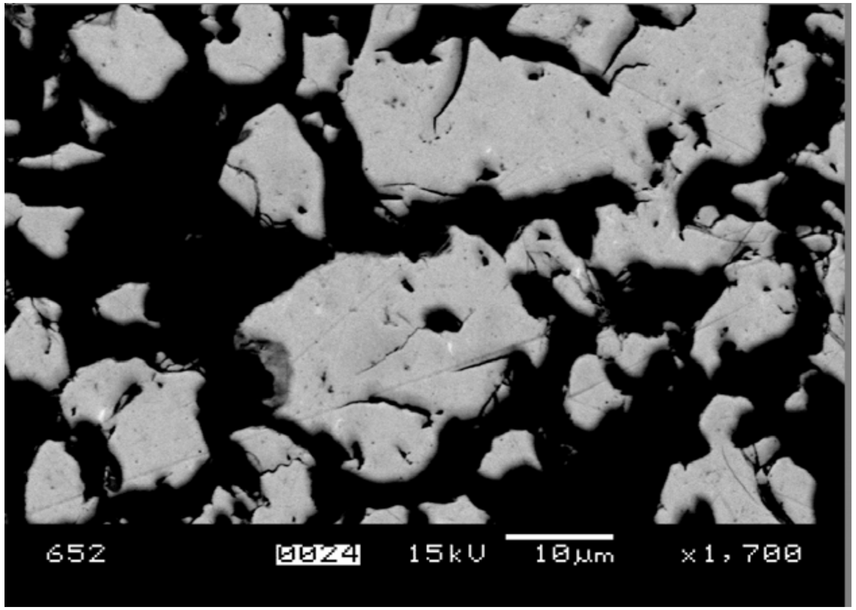
SEM: $SmCo_5$ + 20% α-Fe

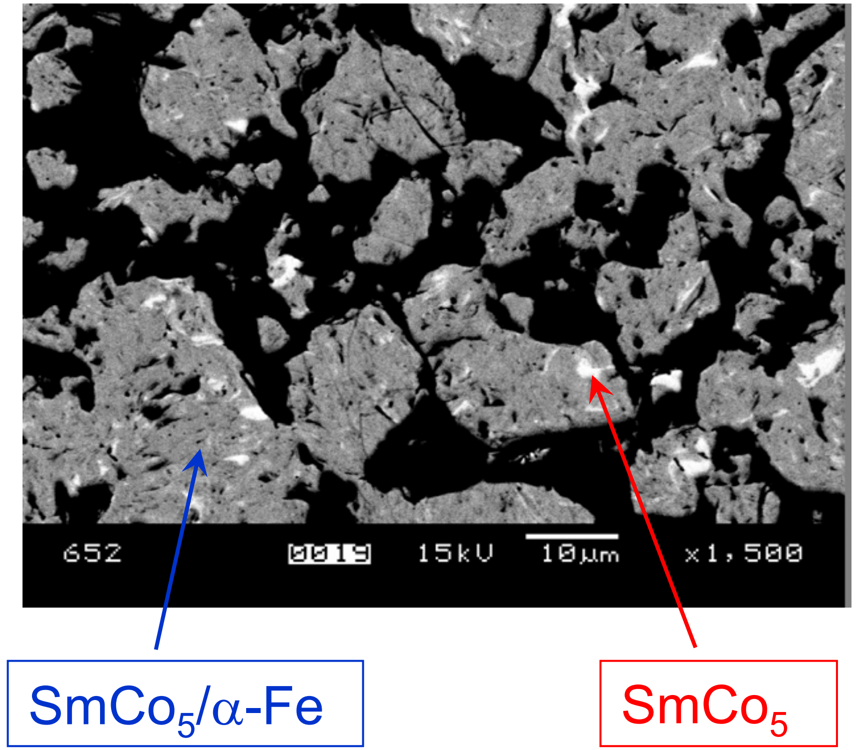
Milling time ◄► Composite homogeneity



6 h milled samples annealed at 600 °C

8 h milled sample annealed at 550 °C



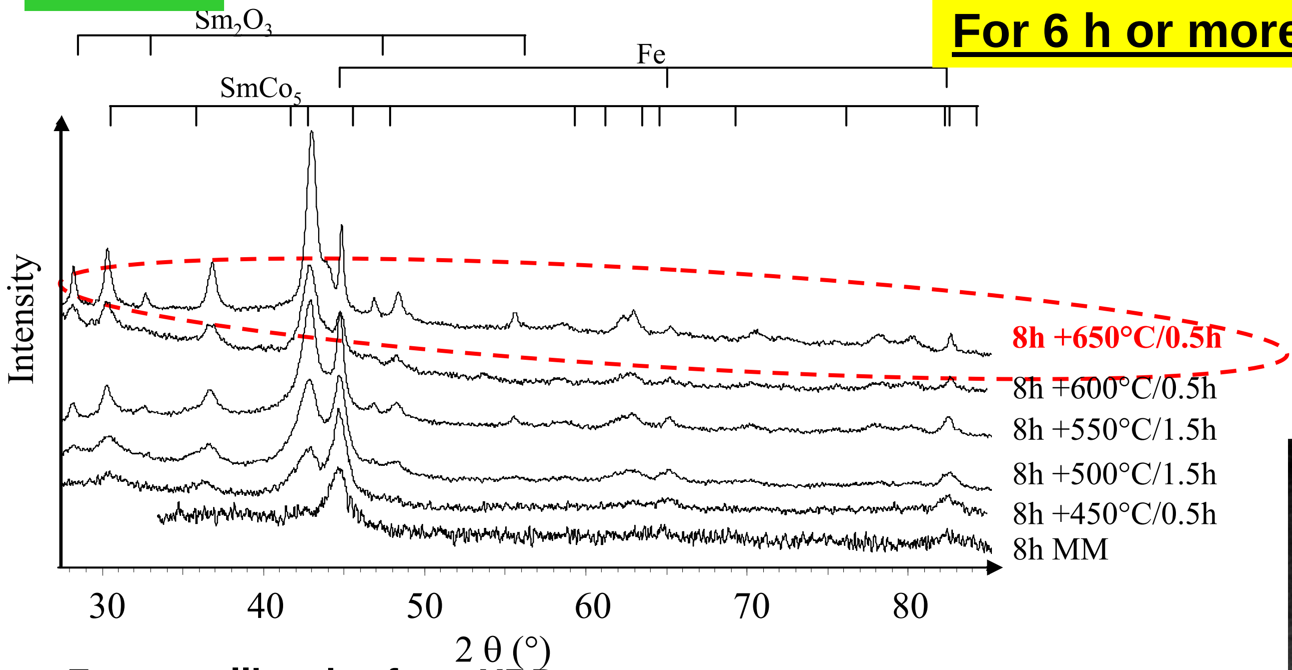


$SmCo_5$ + 20% α-Fe

Milling + Annealing ◀▶ Crystallites dimension

XRD:

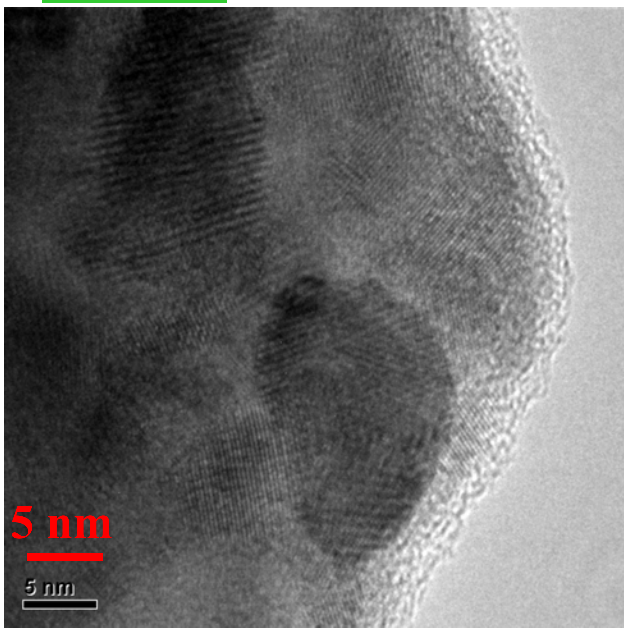
For 6 h or more MM sample D < 30 nm



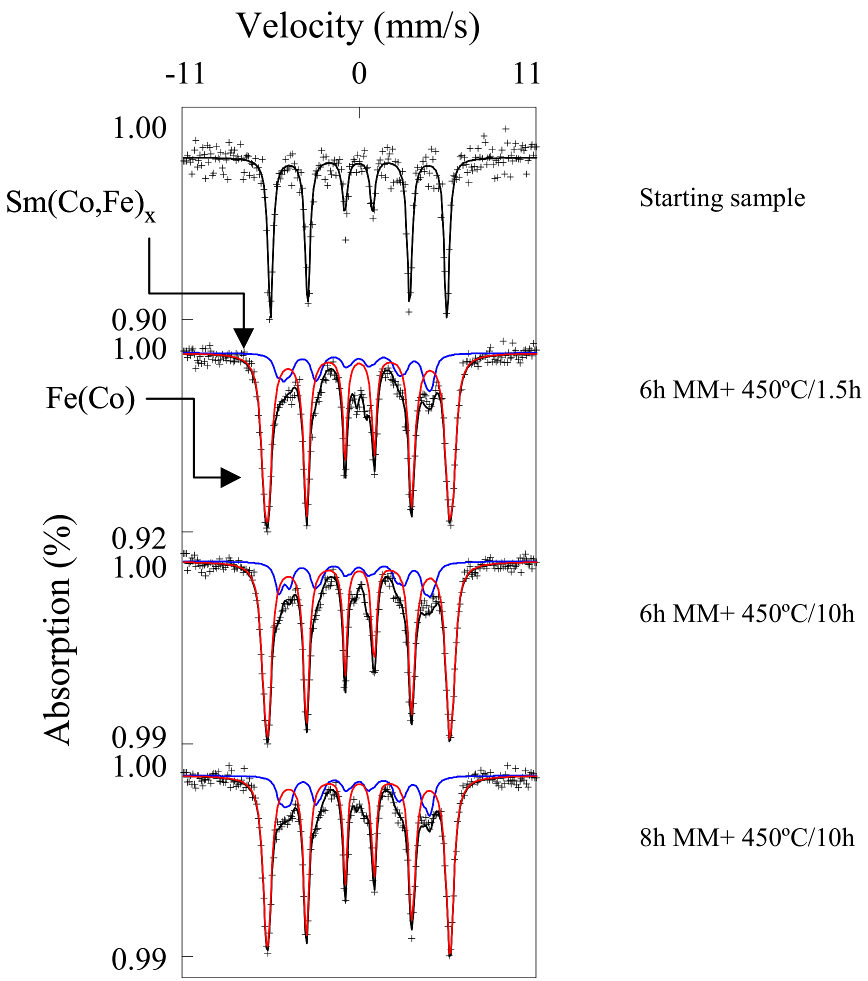
Fe crystallite size from XRD

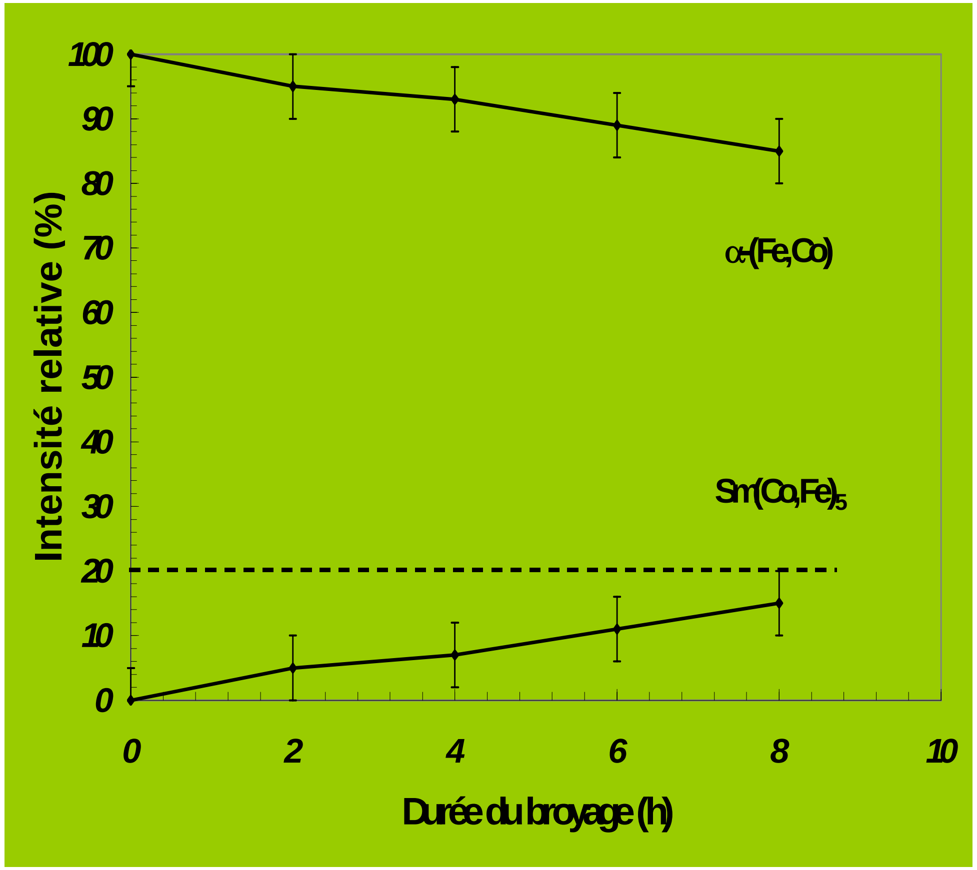
Annealing Temperature (°C)/(time)	$(Pr_{0.92}Dy_{0.08})_2Fe_{14}B$ /α-Fe-6hMM (nm)	$(Pr_{0.92}Dy_{0.08})_2Fe_{14}B$ /α-Fe-12hMM (nm)	$(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ /α-Fe-6hMM (nm)
550 (1.5 h)	**20.3**	**17.7**	**16.2**
600 (1.5 h)	**21.6**	**-**	**-**
650 (1.5 h)	**24.4**	**29.4**	**26.4**
800 (5 min)	**33.2**	**33.5**	**36.6**

TEM 6h MM+450 ºC/0.5h



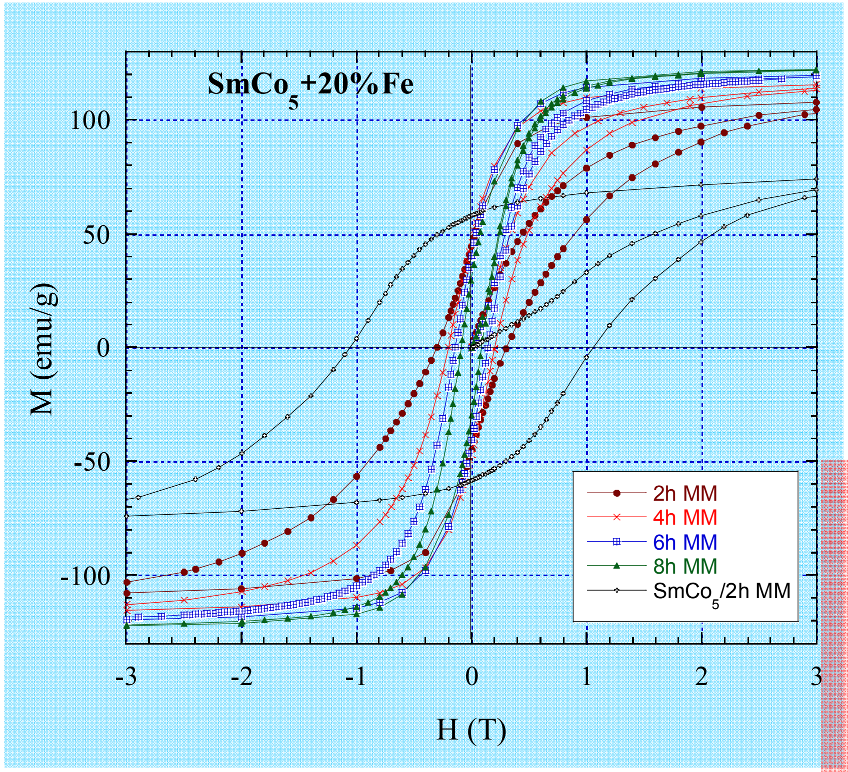
$SmCo_5$ + 20% α-Fe
Fe Mössbauer spectroscopy: Co in Fe and Fe in $SmCo_5$?





α-Fe phase contribution, with the possible insertion of Co in Fe structure, named **α-(Fe,Co)** phase
the second one, different to α-Fe, is given by a **$Sm(Co,Fe)_5$**

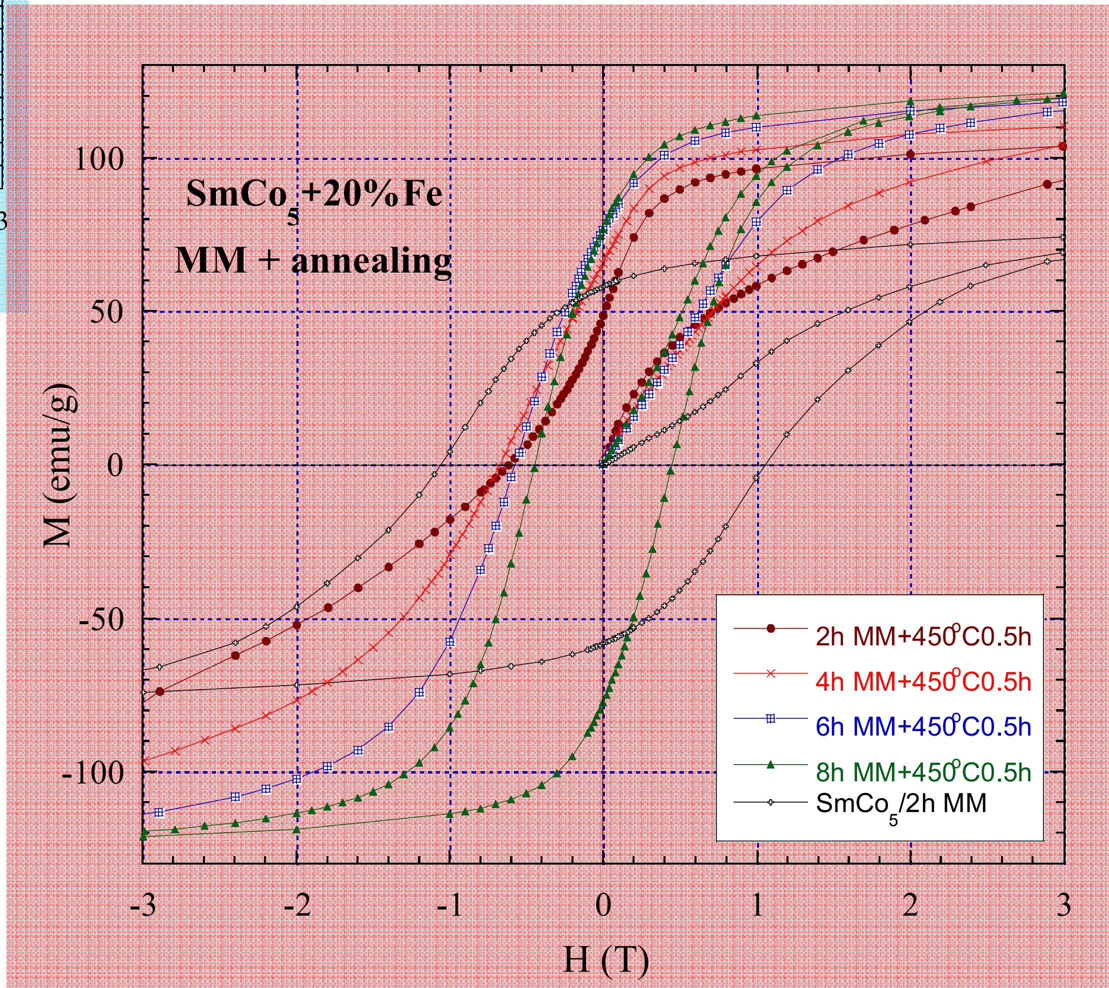
V. Pop, O. Isnard, I. Chicinas, D. Givord, J.M. Le Breton, J. of Optoelectron. Adv. Mater. 8 (2006) 494.
J.M. Le Breton, R. Lardé, H. Chiron, V. Pop, D. Givord, O. Isnard, I. Chicinas, J. Phys. D: App.Phys. (2010)



as milled samples

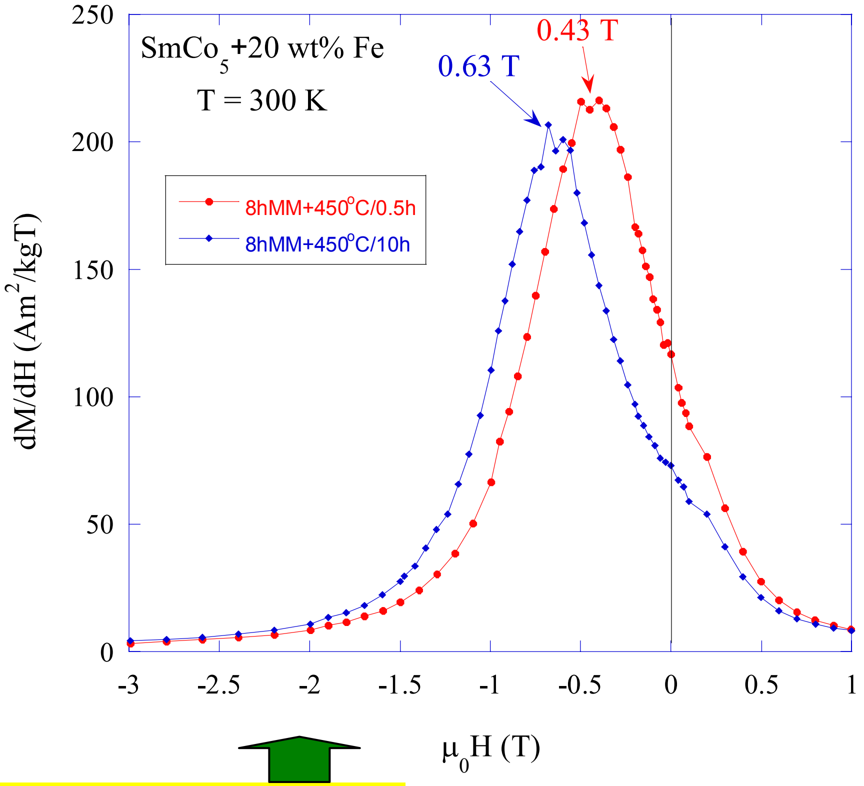
The coercivity and the remanence highly increase with the heat treatment compared to the as milled samples.

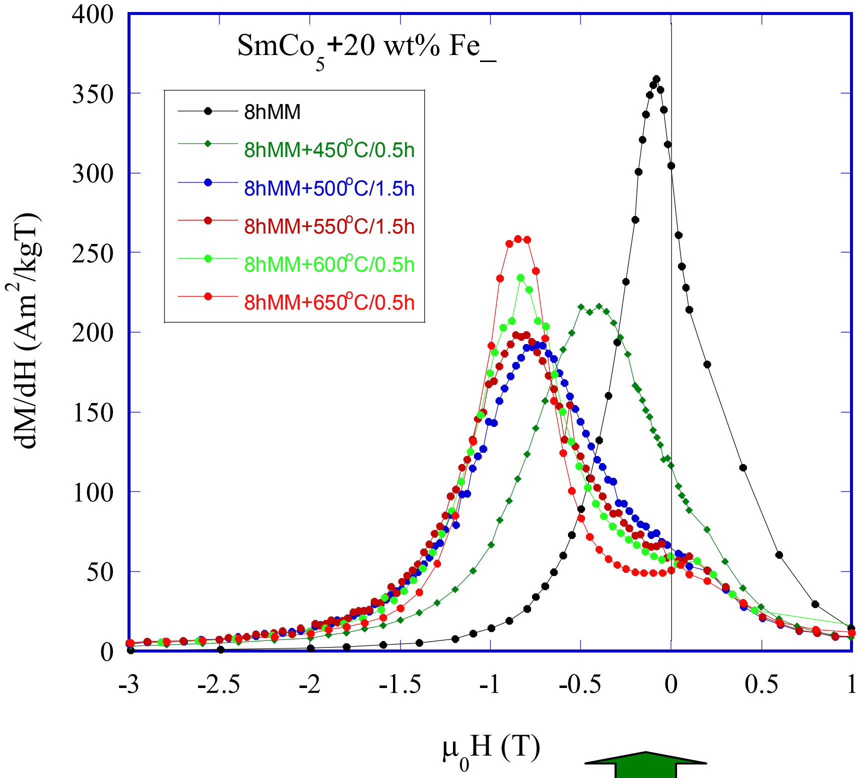
milled and annealed



the influence of the annealing

V. Pop, O. Isnard, I. Chicinas, D. Givord, J.M. Le Breton, J. of Optoelectron. Adv. Mater. 8 (2006) 494.

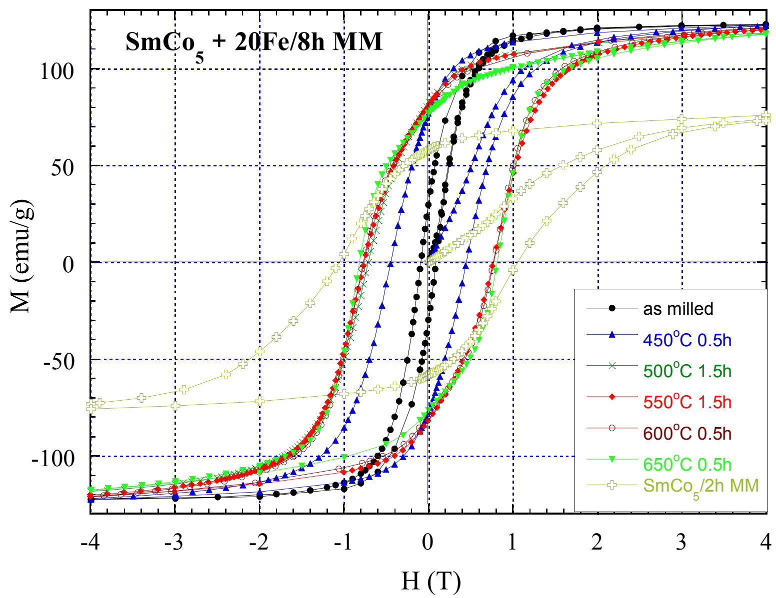




annealing **time**

↕

exchange coupling

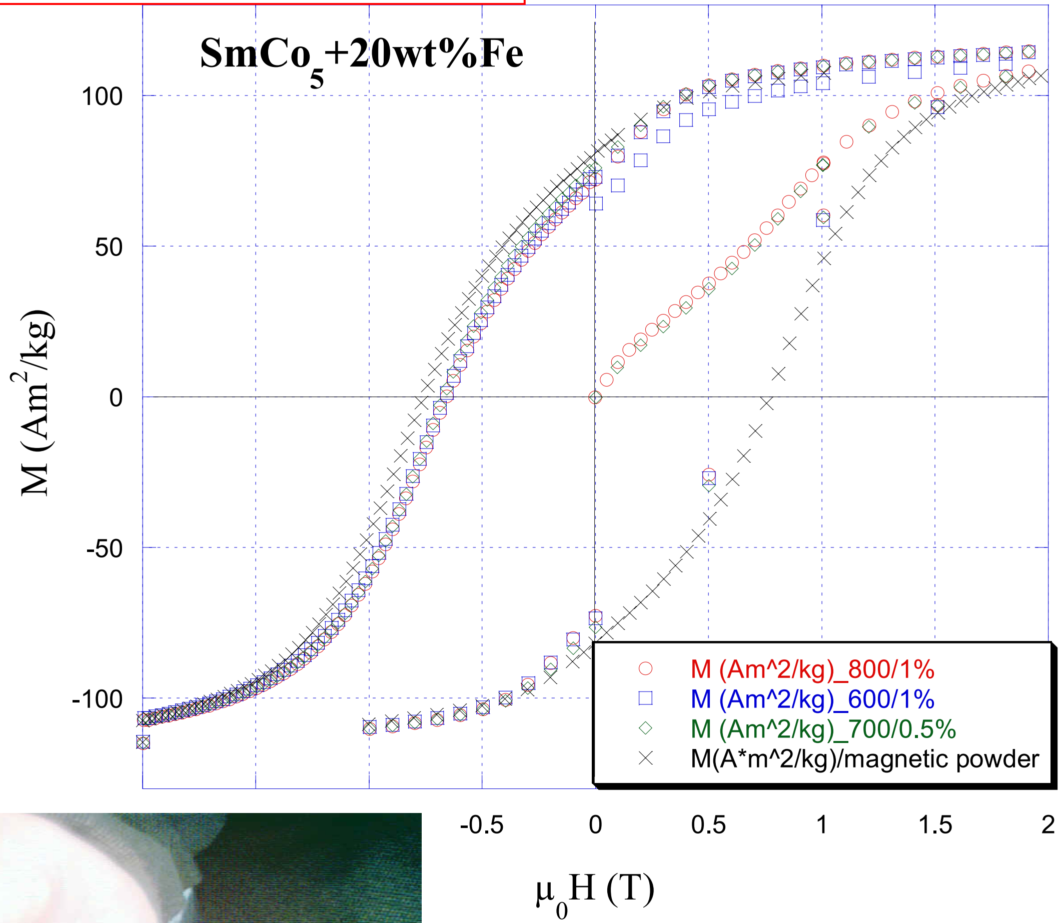


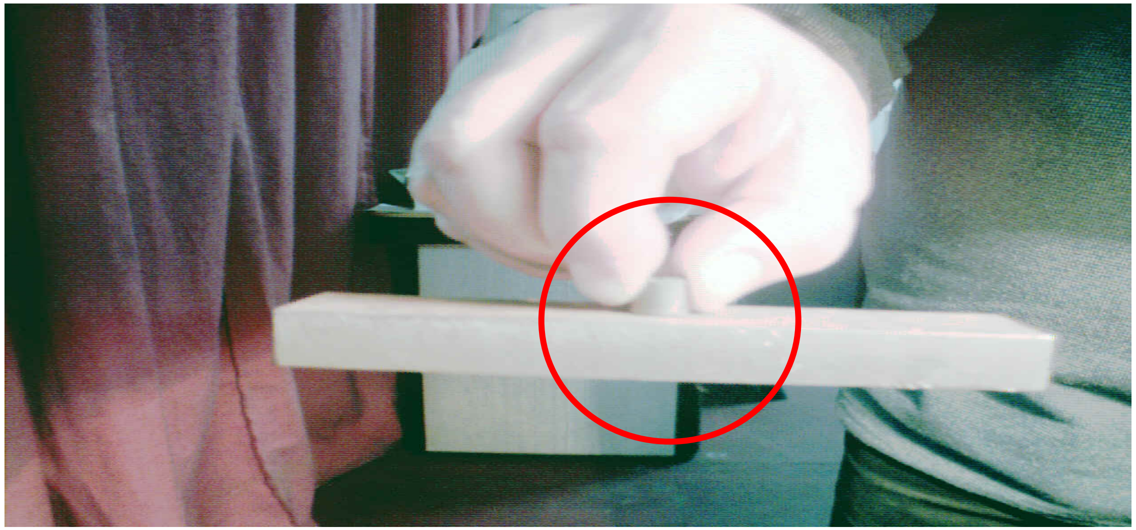
annealing **temperature**

↕

exchange coupling

isotropic bonded magnets ↔ magnetic powder





Research in progress:

Obtaining of bulk spring magnets by SPARK PLASMA SINTERING from mechanically milled powders

II. Soft Magnetic Nanocrystalline Materials

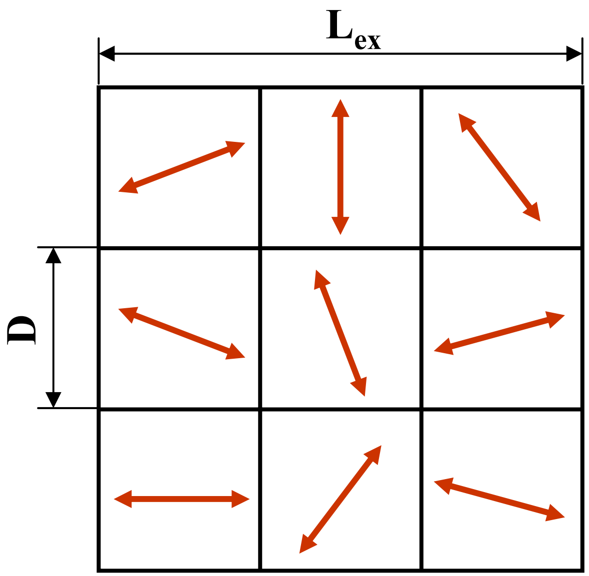
soft magnetic nanostructures

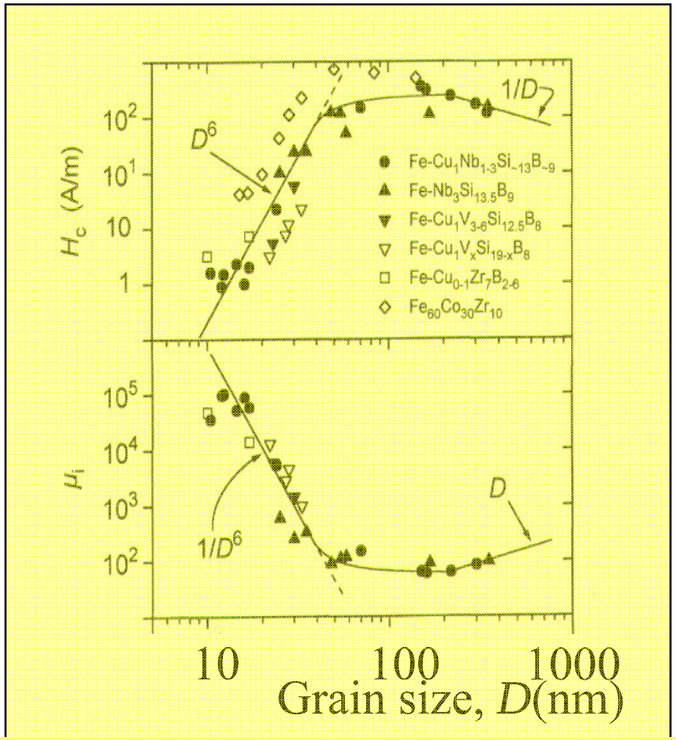
Random Anisotropy Model: $D < L_{ex}$*

small ferromagnetic crystallites **coupled** by exchange interactions

low coercivity and high permeability

The local anisotropies are randomly averaged out by exchange interactions so that there is no anisotropy net effect on the magnetisation process.





* **G. Herzer,** IEEE Trans. Magn. MAG-26 (1990) 1397
R. Alben, J.J. Becker, M.C. Chi, J. Appl. Phys, 49 (1978) 1653

II. Soft Magnetic Nanocrystalline Materials

Ni_3Fe
Supermalloy (9Ni16Fe5Mo , 77Ni14Fe5Cu4Mo, wt%)
Rhometal (64Fe36Ni, wt%)
Hipernick (50Fe50Ni wt%)
Mumetal (76Ni17Fe5Cu2Cr, wt%)

In progress

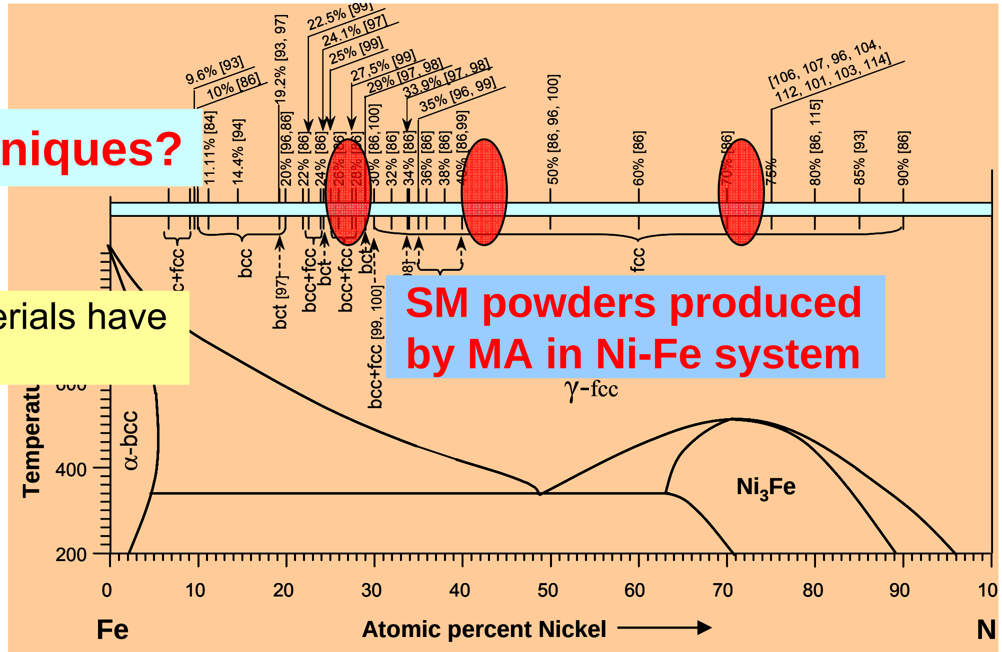
Why Ni-Fe and Ni-Fe-X-(Y) systems?

Why mechanical alloying techniques?

Polycrystalline Ni-Fe and Ni-Fe-X Alloys have very good SMP

Nanocrystalline materials have very good SMP

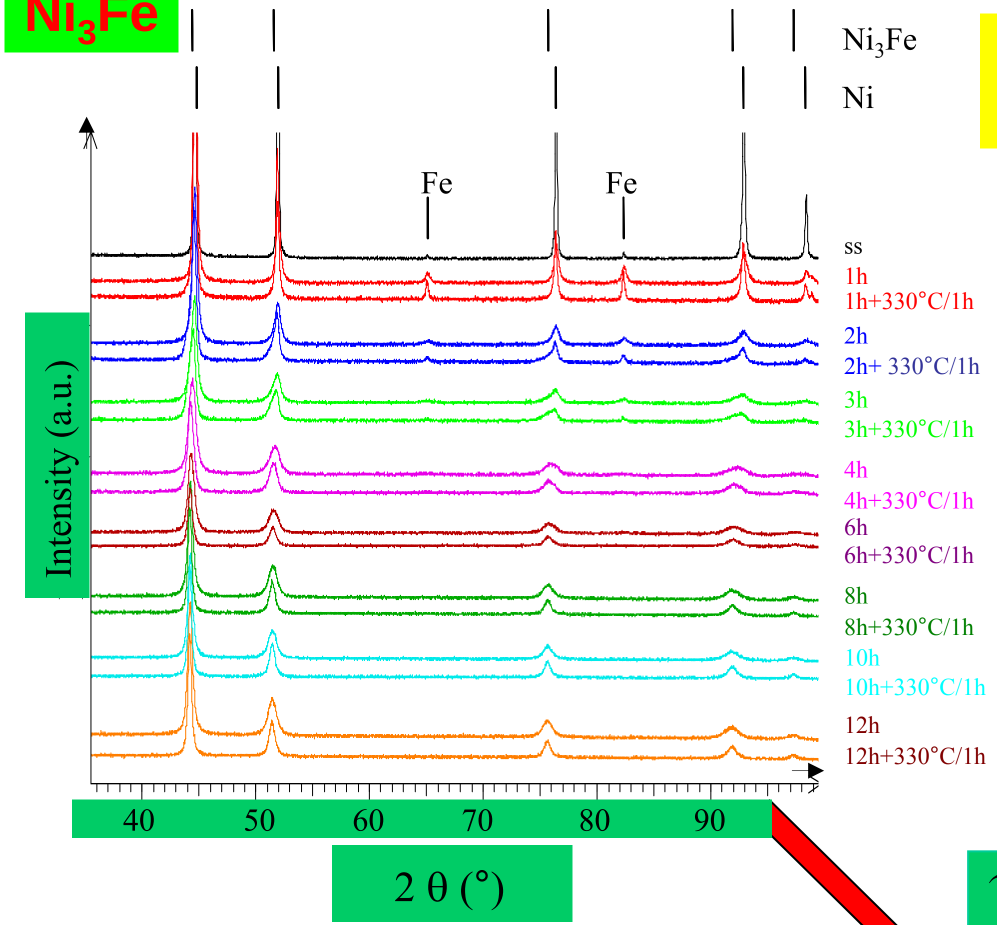
It is possible to combine the properties of Ni-Fe and Ni-Fe-X-(Y) systems with the properties of nanocrystalline state



SM powders produced by MA in Ni-Fe system

I. Chicinaş, , J. Optoelectron. Adv. Mater. **8** (2006), 439-448
V. Pop, I. Chicinaş, J. Optoelectron. Adv. Mater. **9** (2007), 1478-1491

Ni_3Fe

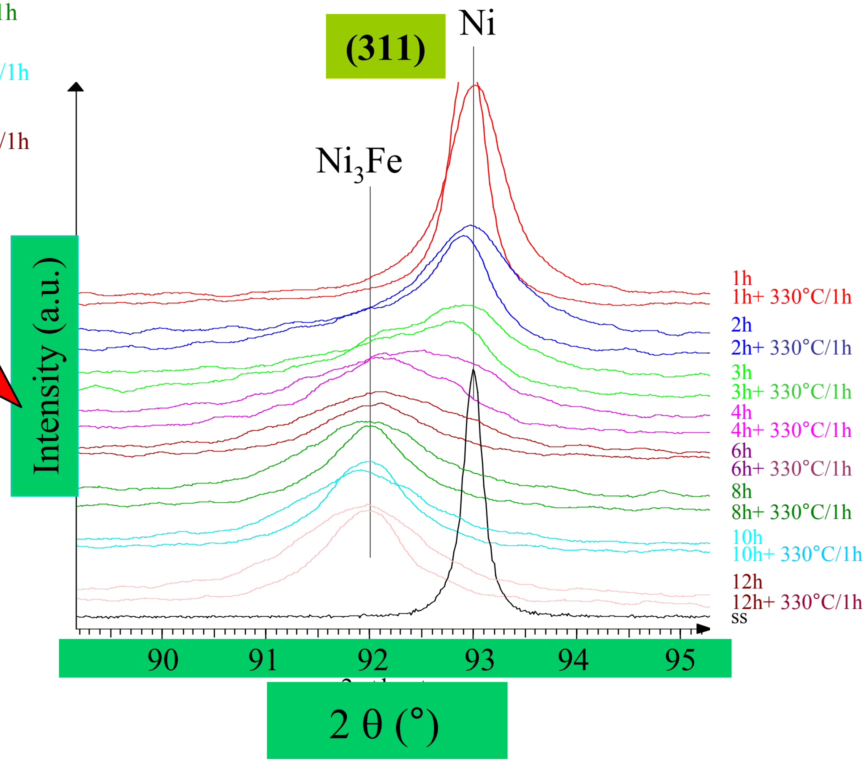


•**Ni_3Fe** phase formation
•the **first order** internal stresses

peaks shift to **lower** 2θ angles

peaks shift to **HIGHER** 2θ angles

relaxation of the first order internal stresses



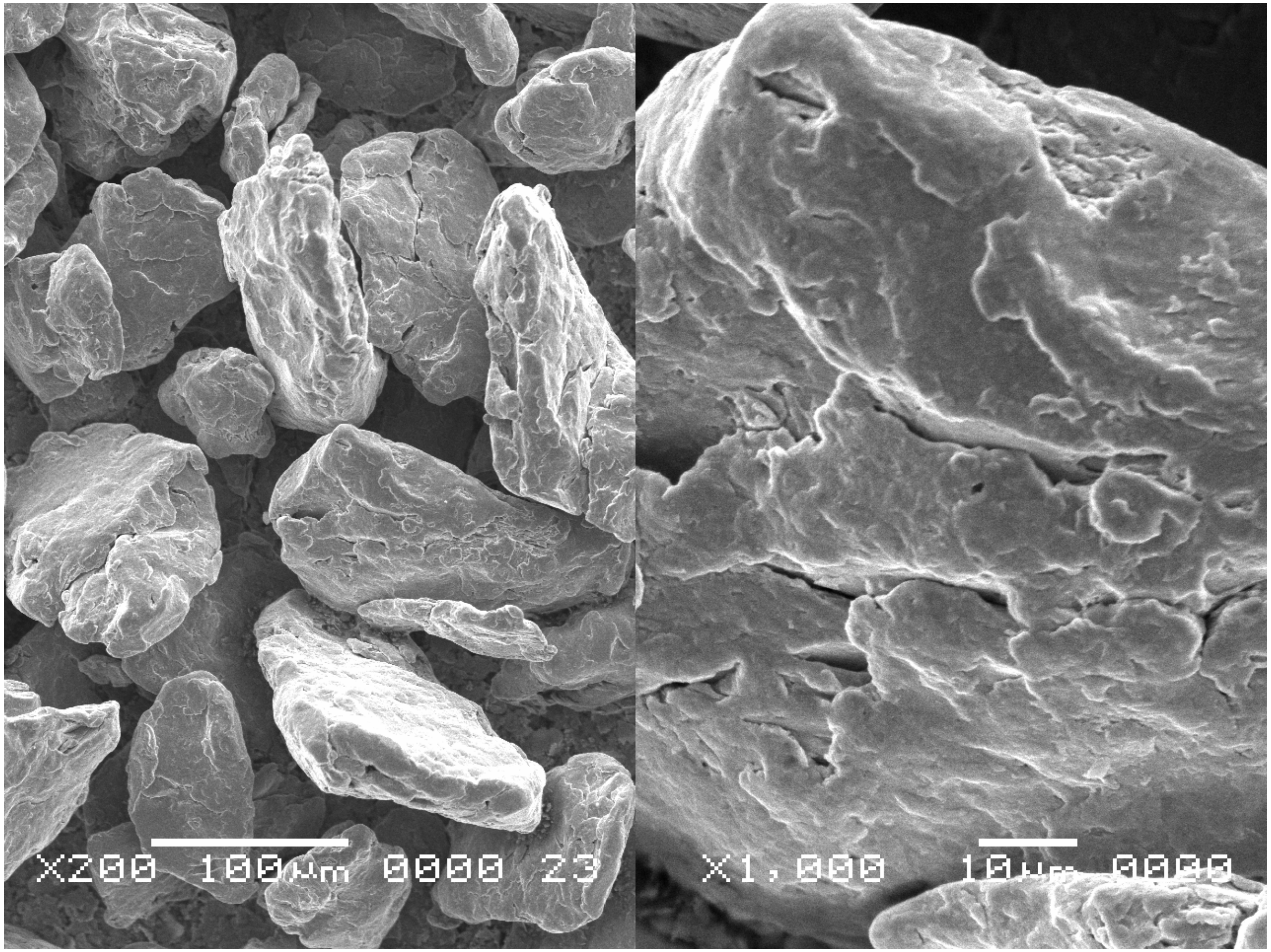
the **second order** internal stresses

broadening of the diffraction peaks

decreasing of the **crystallites dimension**

II. Soft Magnetic Nanocrystalline Materials

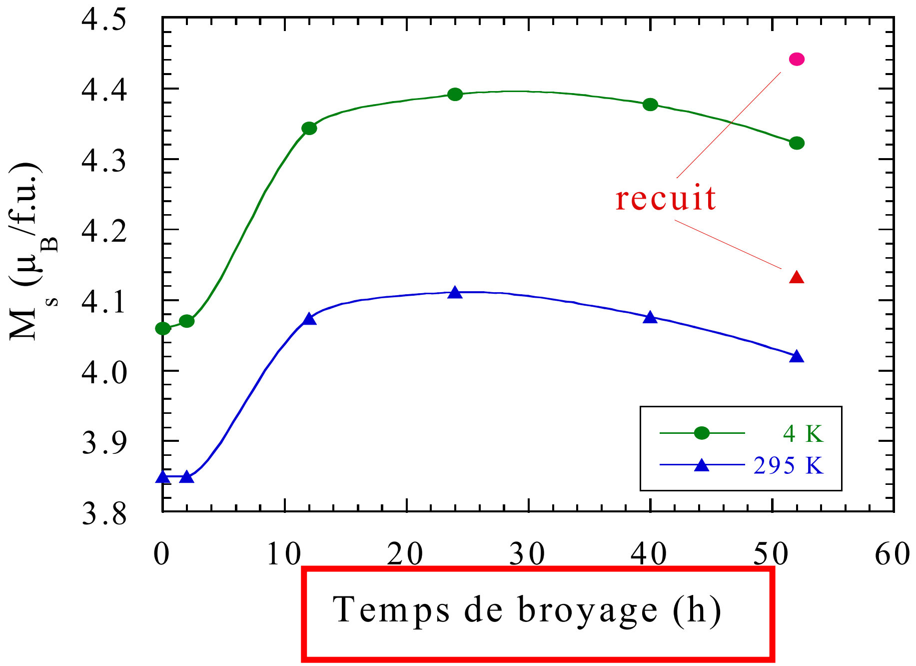
SEM



The particles morphology of the Ni_3Fe powders after 12h mechanical alloying.

II. Soft Magnetic Nanocrystalline Materials

Magnetic measurements

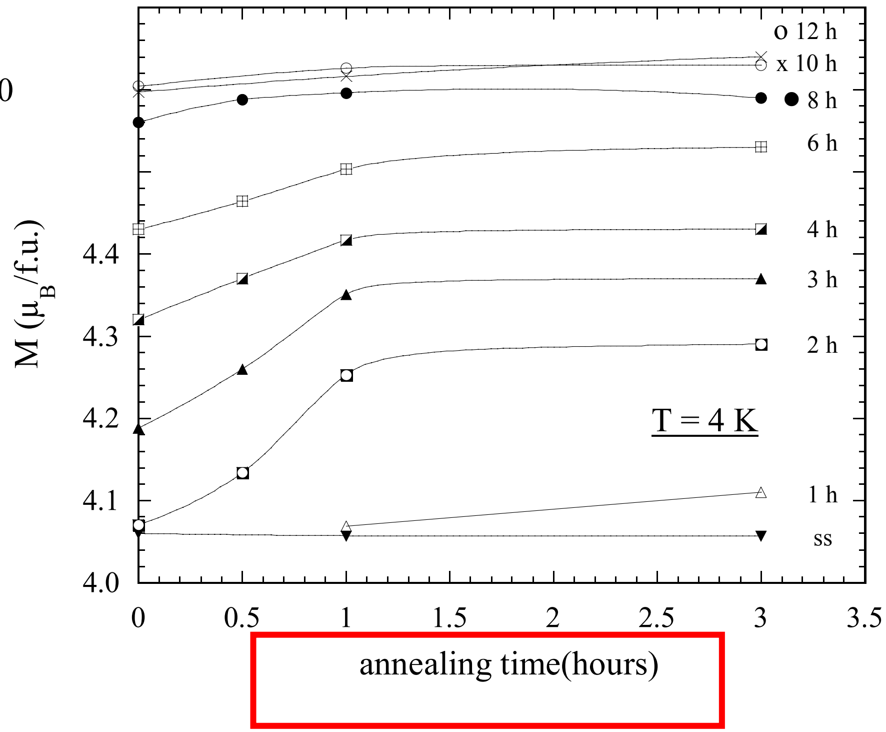


I. Chicinas, V. Pop and O. Isnard,
J. Magn. Magn. Mater. **242-245** (2002) p. 885-887

$Fe_{1-x}Ni_x$
in the reach nickel region*

x ↗ M_{Fe} ↗ and M_{Ni}=ct.

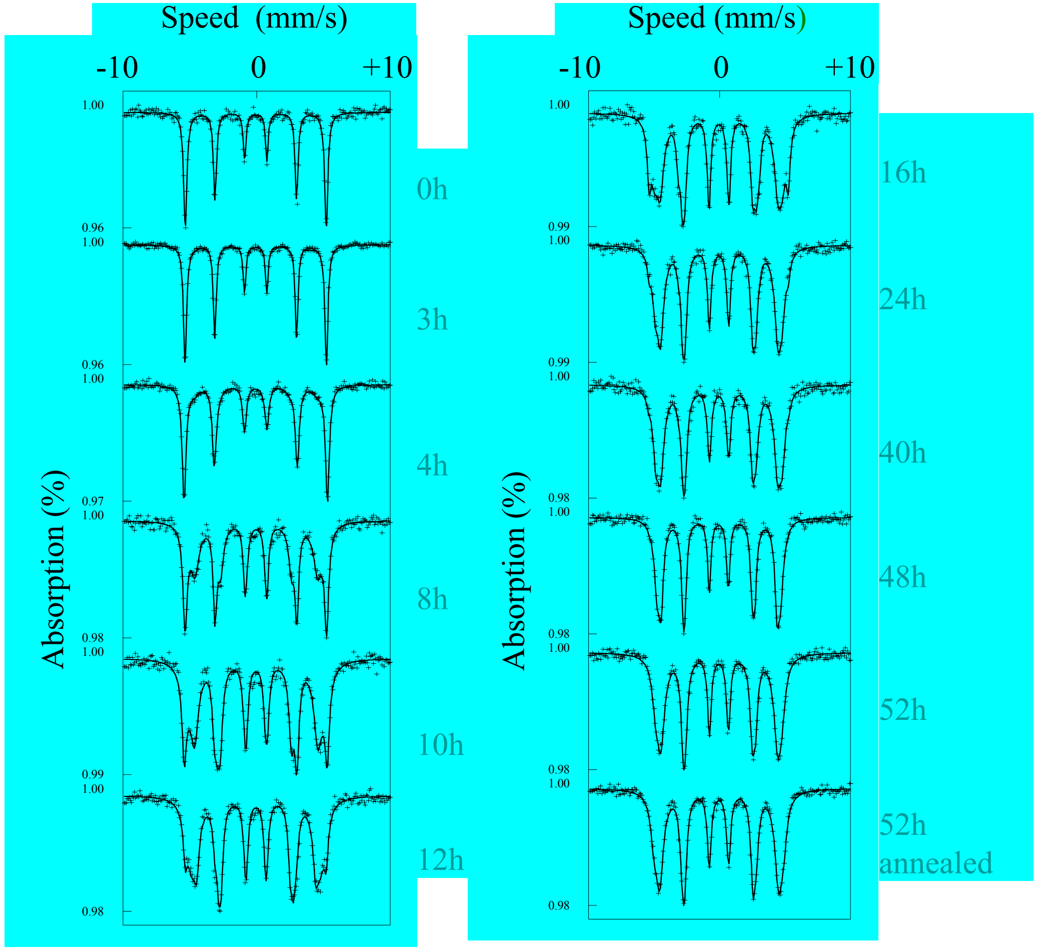
M_{Ni-Fe} ↗ when Ni_3Fe % ↗

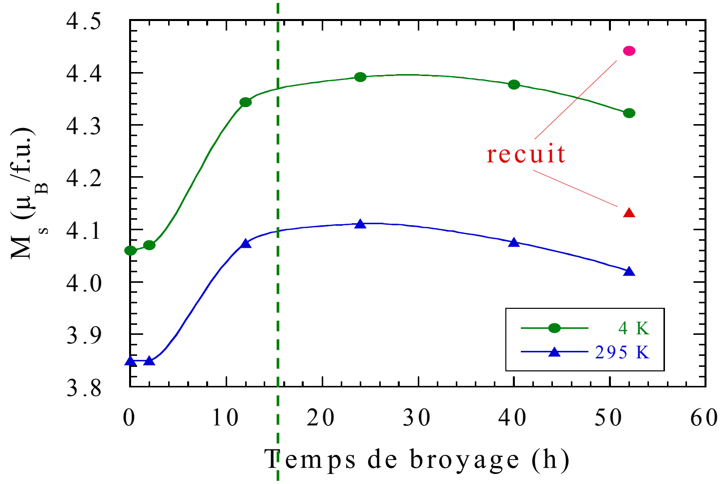


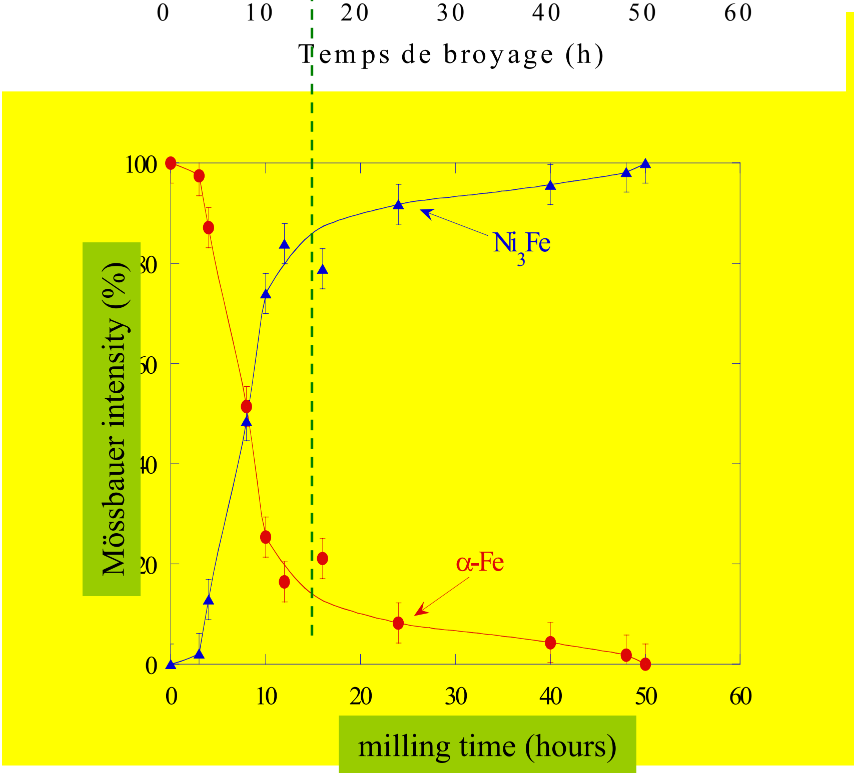
*H. Hasegawa, J. Kanamori, J. Phys. Soc. Jap. **33** (1972) 1599

V. Pop, O. Isnard and I. Chicinas,
J. Alloys and Comp., **361** (2003), p.144-152.

II. Soft Magnetic Nanocrystalline Materials







Mössbauer spectrometry

Ni_3Fe powders

I. Chicinas, V. Pop, O. Isnard, J.M. Le Breton and J. Juraszek, J. Alloys and Compounds 352 (2003), p. 34-40

Some results

77Ni14Fe5Cu4Mo wt%

10h : one T_c is observed by heating

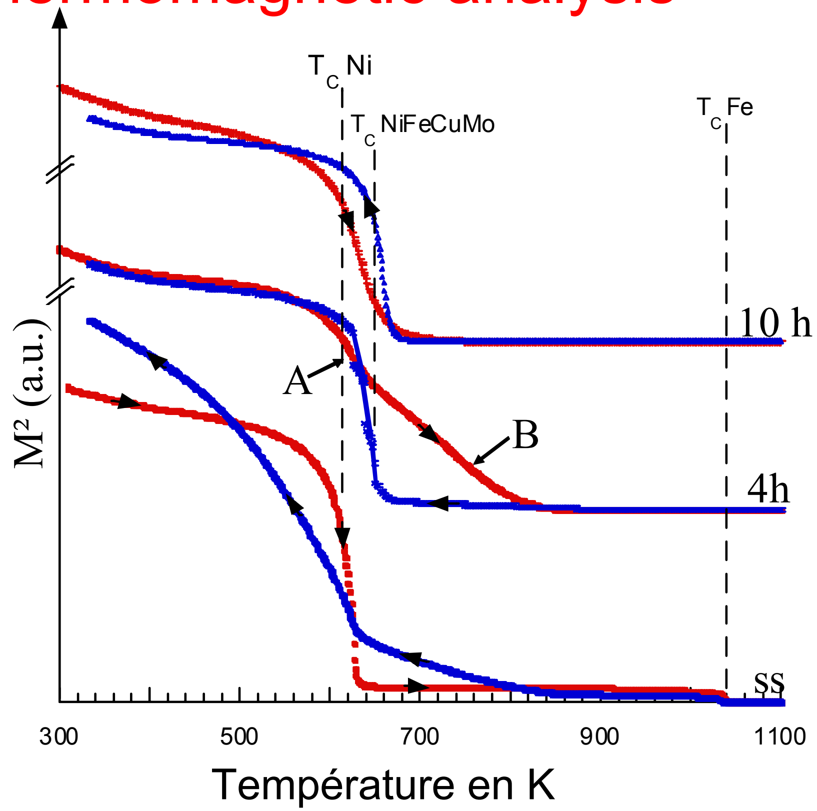
4h : - by heating, point A correspond to T_c of NiFeCuMo obtained by milling

- progressive formation of the alloys by heating, B region.

-at cooling, only one magnetic phase, T_c

SS : start mixture: T_c of Ni and Fe

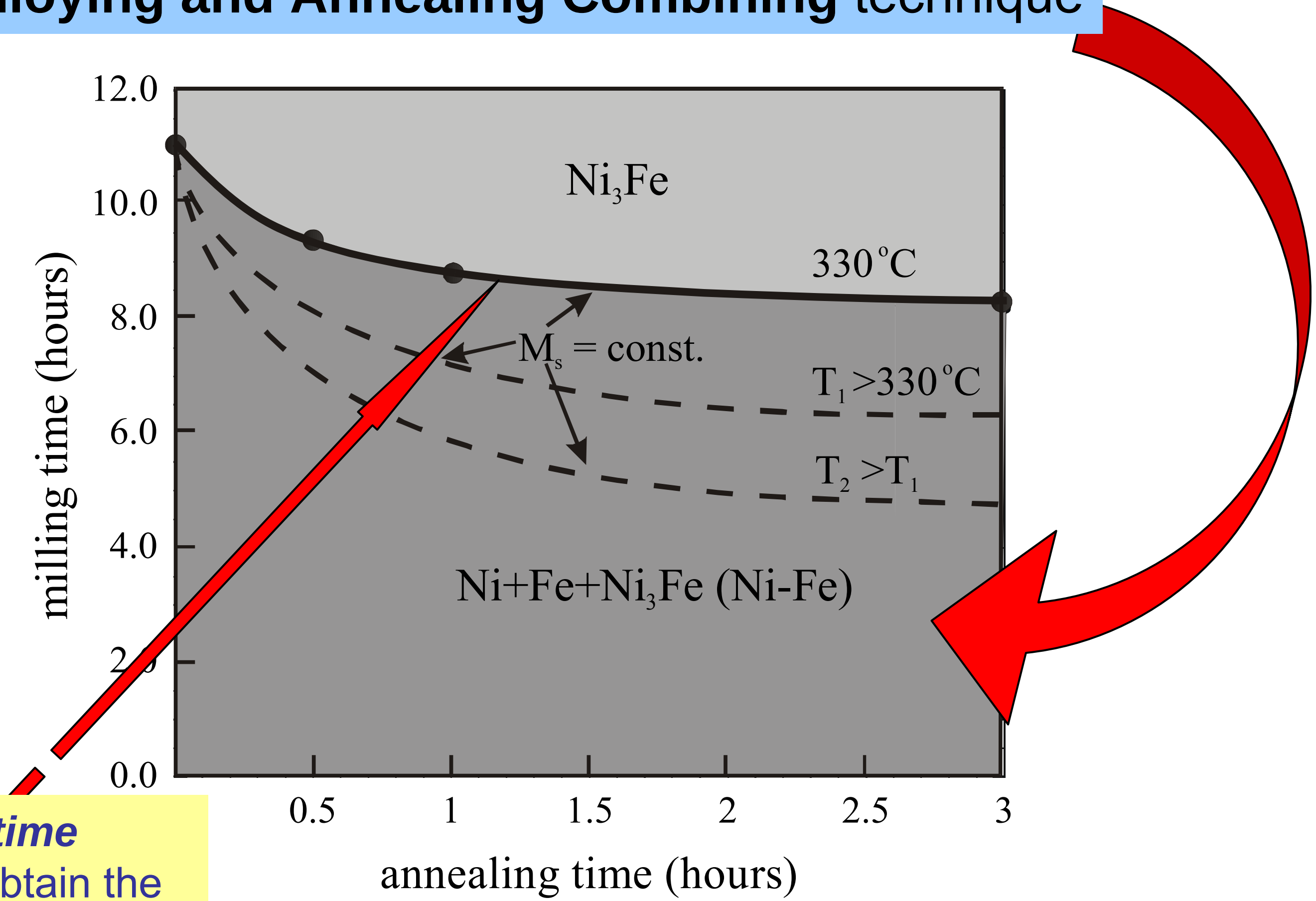
thermomagnetic analysis



F. Popa, O. Isnard, I. Chicinas, V. Pop, J. Magn. Magn. Mater., 316 (2007) e900–e903
F. Popa, O. Isnard, I. Chicinas, V. Pop, J. Magn. Magn. Mater., (2010) in press

II. Soft Magnetic Nanocrystalline Materials

Mechanical Alloying and Annealing Combining technique



milling time–annealing time combination required to obtain the Ni_3Fe phase in the whole sample

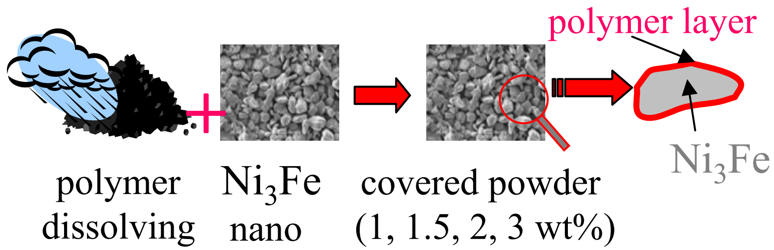
Milling – Annealing - Transformation (MAT) diagram

V. Pop, O. Isnard and I. Chicinas, J. Alloys and Comp., **361** (2003), p.144-152.

Some results

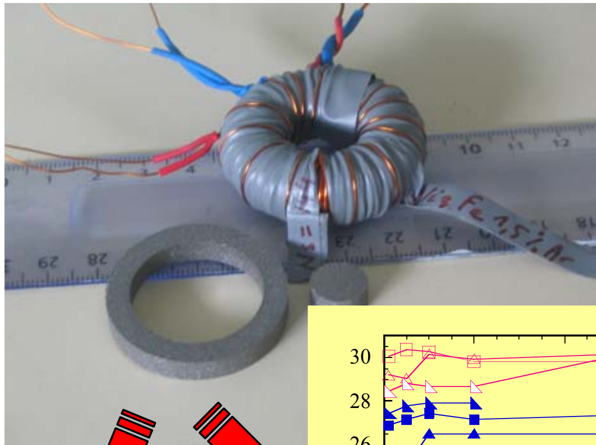
Soft magnetic nanocrystalline composites

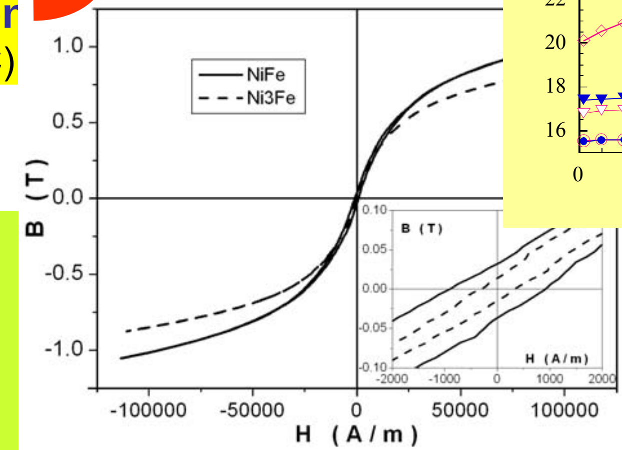
Composites Production

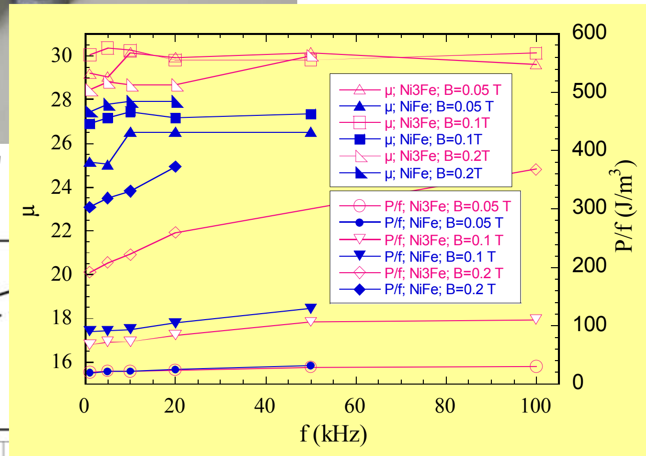


Die pressed (600 - 800 MPa)

Polymerisation (60 min., 180 °C)







Research in progress:

Obtaining of nanocrystalline compacts by SPARK PLASMA SINTERING from mechanically alloyed powders

I. Chicinaş, O. Isnard, O. Geoffroy, V. Pop, J. Magn. Magn. Mater. **290-291** (2005), 1531-1534
I. Chicinaş, O. Isnard, O. Geoffroy, V. Pop, J. Magn. Magn. Mater. **310** (2007), 2474-2476

Thank you

Mulțumesc