Soft magnetic nanocrystalline/nanostructured materials produced by mechanical alloying routes

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Research of our group are centred on:

(i)soft magnetic nanocrystalline metallic powders produced by mechanical alloying;

(ii) soft magnetic nanocomposite powders like $MeFe_2O_4$/(Fe-Ni, Ni-Fe-X) produced by mechanical milling;

(iii) soft magnetic nanocrystalline composite materials and

(iv) soft magnetic nanocrystalline compacts produced by Spark Plasma Sintering from mechanically alloyed powders.

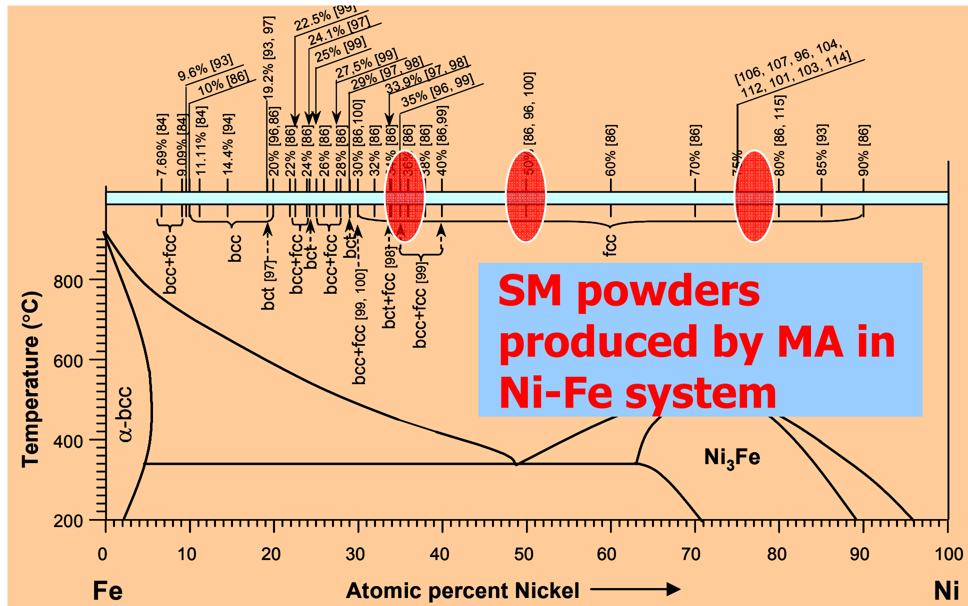
Why Ni-Fe (or Ni-Fe-X-Y) systems?

Why mechanical alloying techniques?

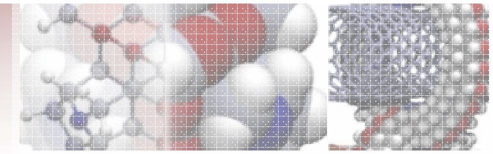
Polycrystalline Ni-Fe and Ni-Fe-X alloys have very good SMP

Nanocrystalline materials have very good SMP

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



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



Why mechanical alloying?

Usually, we make alloys by melting together the components

Mechanical alloying (MA) involves <u>the synthesis</u> of materials in solid state by high-energy ball milling

Mechanical milling (MM): powder milling without producing chemical reactions; conservation of the initial phases.

Elemental Powders Mixture

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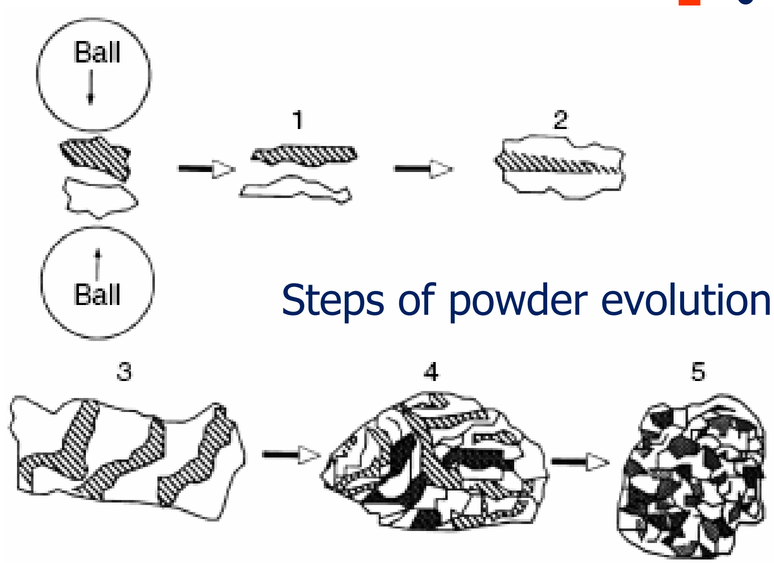
Milling in high energy ball mill

- Particles and grains are fractured
- Defects introduced in particles
- Temperature rise - diffusion

New phase

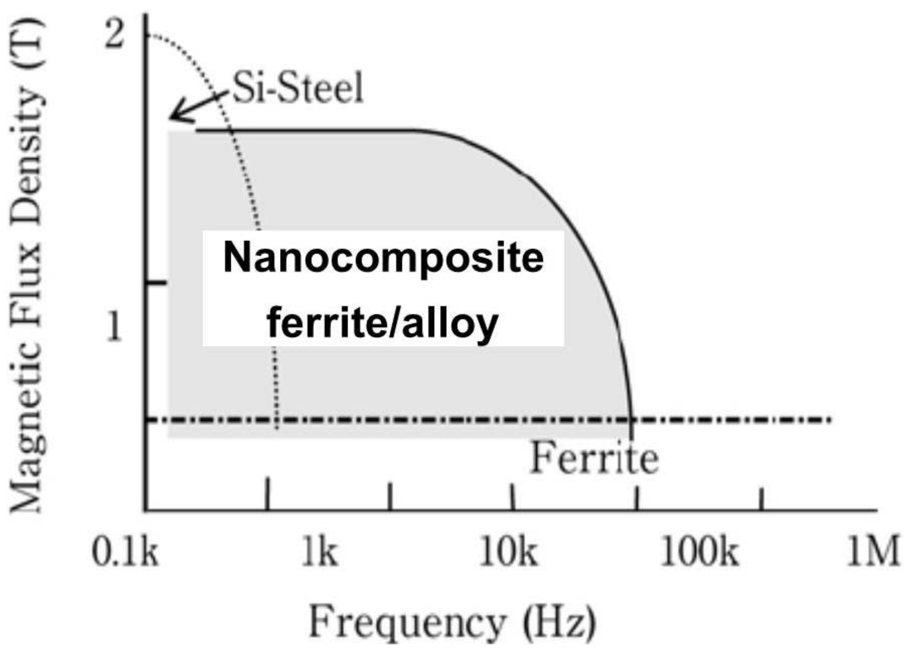


Steps of powder evolution during mechanical alloying.

By MA route we obtain nanocrystalline powders

E. Gaffet, G. Le Caër, *Encyclopedia of Nanoscience and Nanotechnology, E*dited by H.S.Nalwa, Volume X: Pages (1–39)

Why soft magnetic nanocomposite powders like $MeFe_2O_4$/(Fe-Ni, Ni-Fe-X)



EXPERIMENTAL

Compositions:

Powders

Ni_3Fe, Supermalloy (79Ni16Fe5Mo, 77Ni14Fe5Cu4Mo) Mumetal (76Ni17Fe5Cu2Cr), Hipernick (50N50Fe) Rhomtal (36Ni64Fe) (wt%)

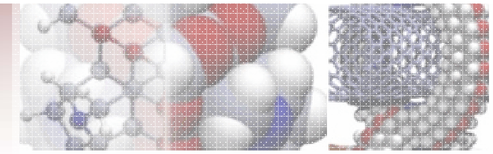
$ZnFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$
$ZnFe_2O_4$/α-Fe, $ZnFe_2O_4$/Ni,
$NiFe_2O_4$/α-Fe, $NiFe_2O_4$/Supermalloy

compacts

SMC: Ni_3Fe+dielectric, Supermalloy+ dielectric
Sintered: Ni_3Fe, Supermaloy+Fe, $NiFe_2O_4$/Supermalloy

Producing

- **Wet or dry mechanical alloying**
  - Ni Carbonil, Fe NC 100.24 (d< 40 µm), Mo obtenu par réduction chimique , Cu – Pometon S.p
  - broyeur planétaire Fritsch, Pulverisette 4,
  - BPR 8:1, Ω = 400; ω = 800, degré de remplissage ≈ 40 %
  - agent de contrôle du processus – Benzène
- **Annealing**(350 °C, 4 heures, sous vide)
- **Soft magnetic composites producing**
- **Spark plasma sintering**

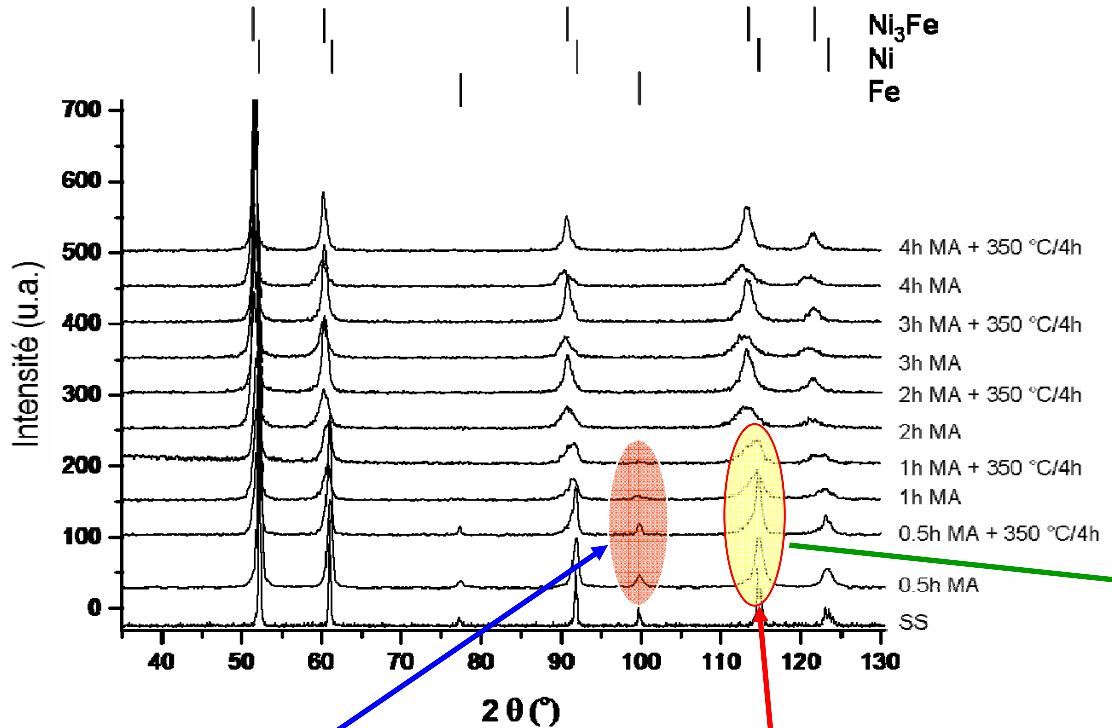


Characterisation :

- **Particle size distribution**(Laser Particle Size Analyzer (Fritsch Analysette 22 – Nanotec)
- **Stuctural: X-ray diffraction, neutron diffraction**
  - diffraction de rayons X – 2θ = 30 – 130 °, longueur d'onde: Co Kα, et Cu Kα,
  - diffraction de neutrons – Institut Laue-Langevin- Grenoble - λ = 1,287 Å, 2θ = 30 – 130 °
- **Morphology and X-ray Microanalysis (SEM+EDX)** (JSM 5600LV-Jeol, Oxford Inst, Logiciel Inca 200)
- **Magnetic measurements**: M = f(H) 0 – 8 T, 4-300 K, DC/AC hysteresis (up to 100kHz)
- **DSC:** 23 – 700 °C , vitesse de chauffage 10 °C/min, atmosphère Ar + 8 % H2
- **IR Spectrometry**(Specord 75 IR (Carl Zeiss Jena) gamme 4000-400 cm-1)
- **Mass Spectrometry and thermogravimetry** (Thermostar SM GSD 301 QMS 200, TGA Q500 (TA instruments Q series)
- **Mössbauer spectrometry**

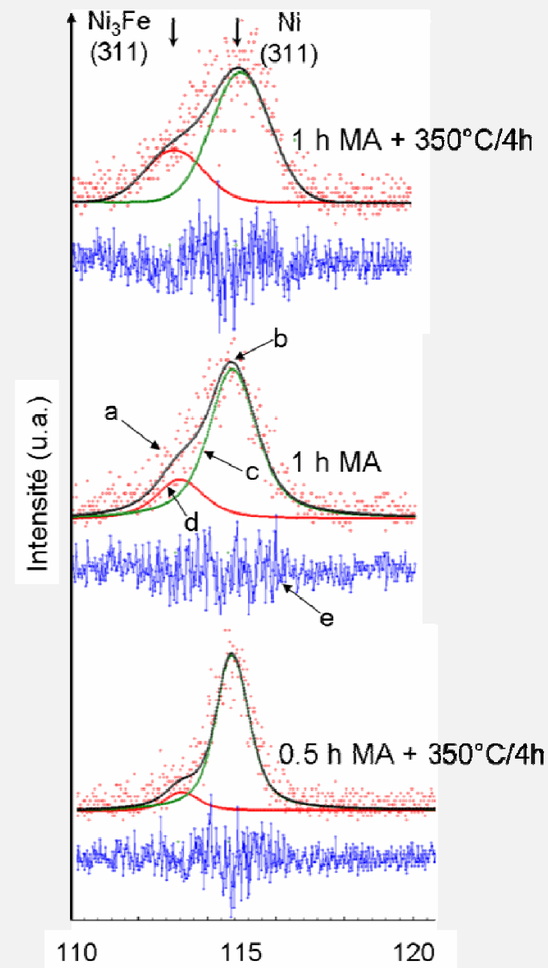
Résultats et discussion – (i) Ni_3Fe

Formation du composé intermétallique Ni_3Fe par broyage <u>mécanique par voie humide</u>



•1 heure de broyage - le pic du fer est encore visible
•1 heure et recuite – le pic du fer n'est plus observée

une asymétrie des pics peut être observée

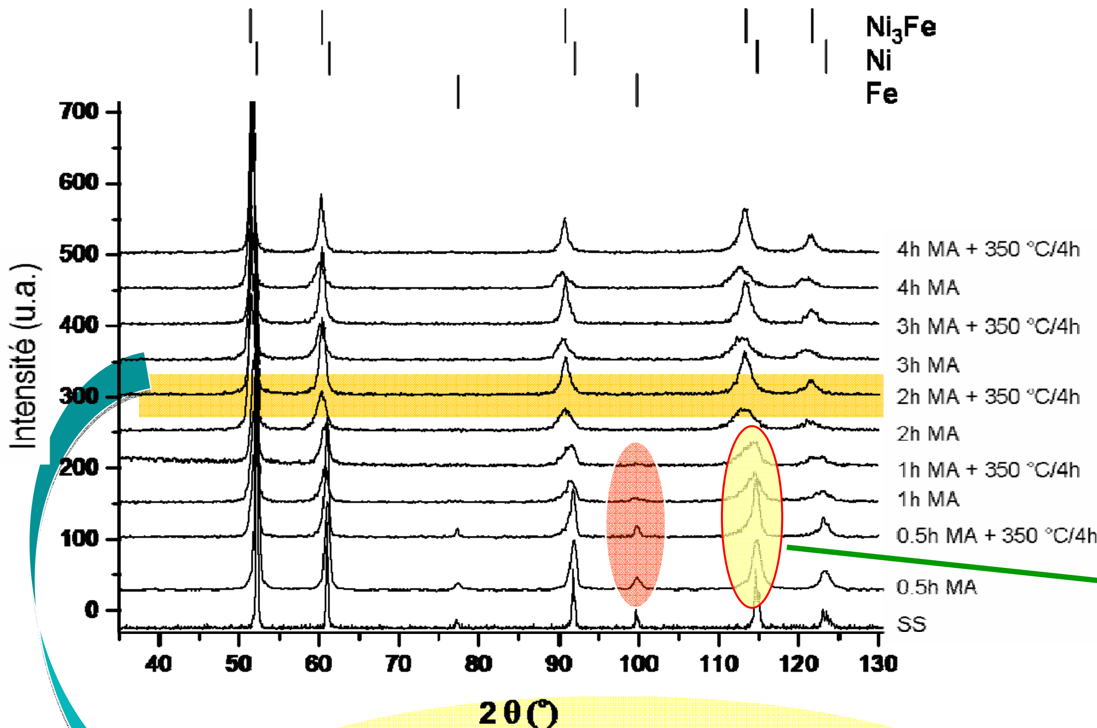


a - les points expérimentaux,
b - la forme expérimentale du pic (311),
c - le pic (311) du Ni obtenue par déconvolution
d - le pic (311) de Ni_3Fe obtenue par déconvolution,
e - la différence entre le spectre expérimental et le spectre calculé.

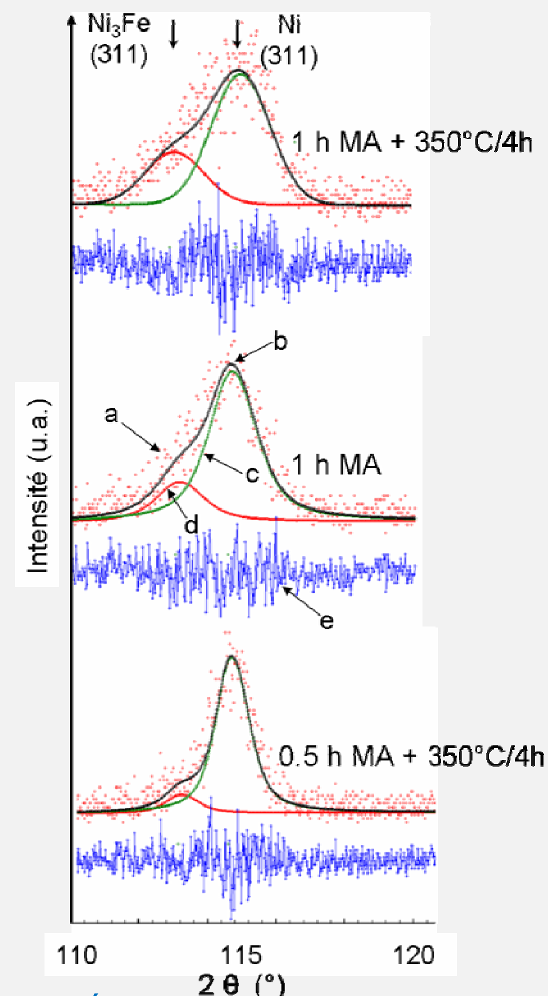
B.V. Neamţu, I. Chicinaş, O. Isnard, F. Popa, V. Pop, *Intermetallics 19 (2011) 19-25*

Résultats et discussion – (i) Ni_3Fe

Formation du composé intermétallique Ni_3Fe par broyage mécanique par voie humide



le composé a été obtenu après 2 heures de broyage mécanique par voie humide et un recuit à la température de 350 °C pendant 4 heures



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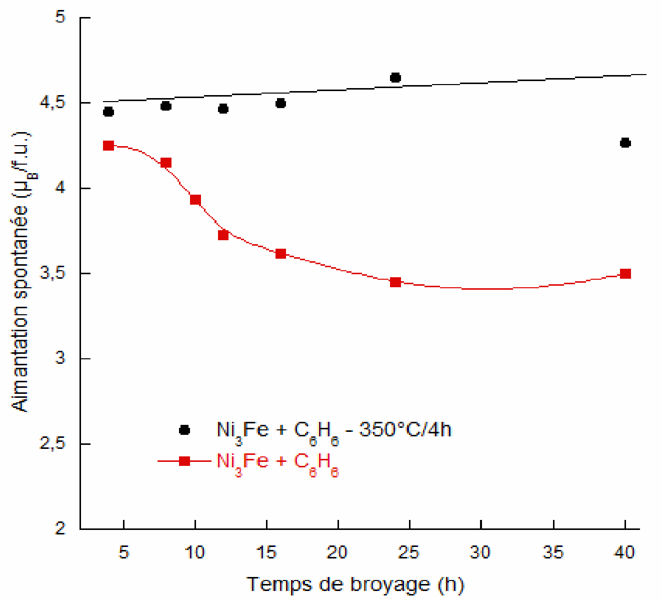
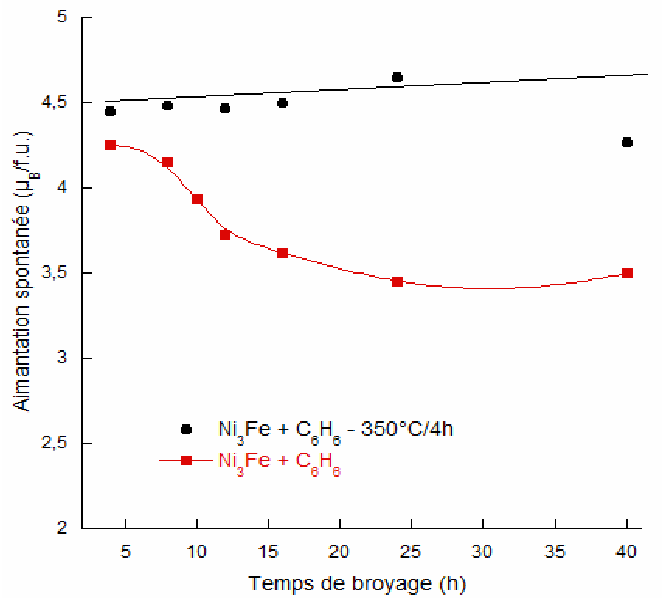
e - la différence entre le spectre expérimental et le spectre calculé.

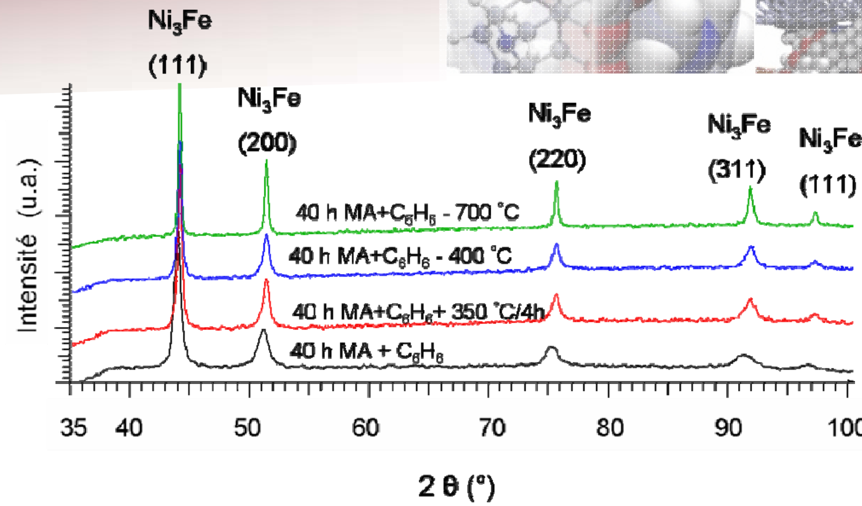
B.V. Neamţu, I. Chicinaş, O. Isnard, F. Popa, V. Pop, *Intermetallics 19 (2011) 19-25*

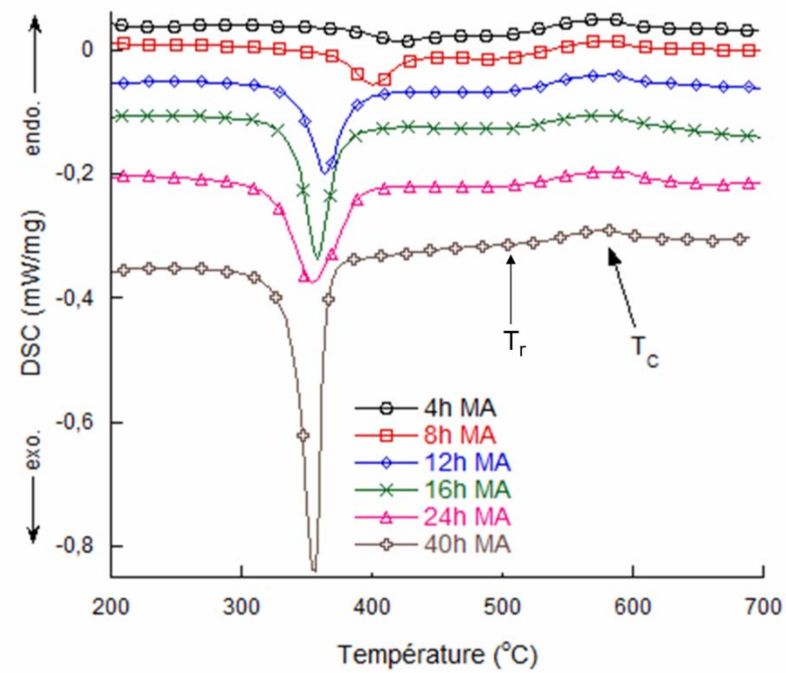
Résultats et discussion – (i) Magnetisation



Résultats et discussion – (i)
DSC





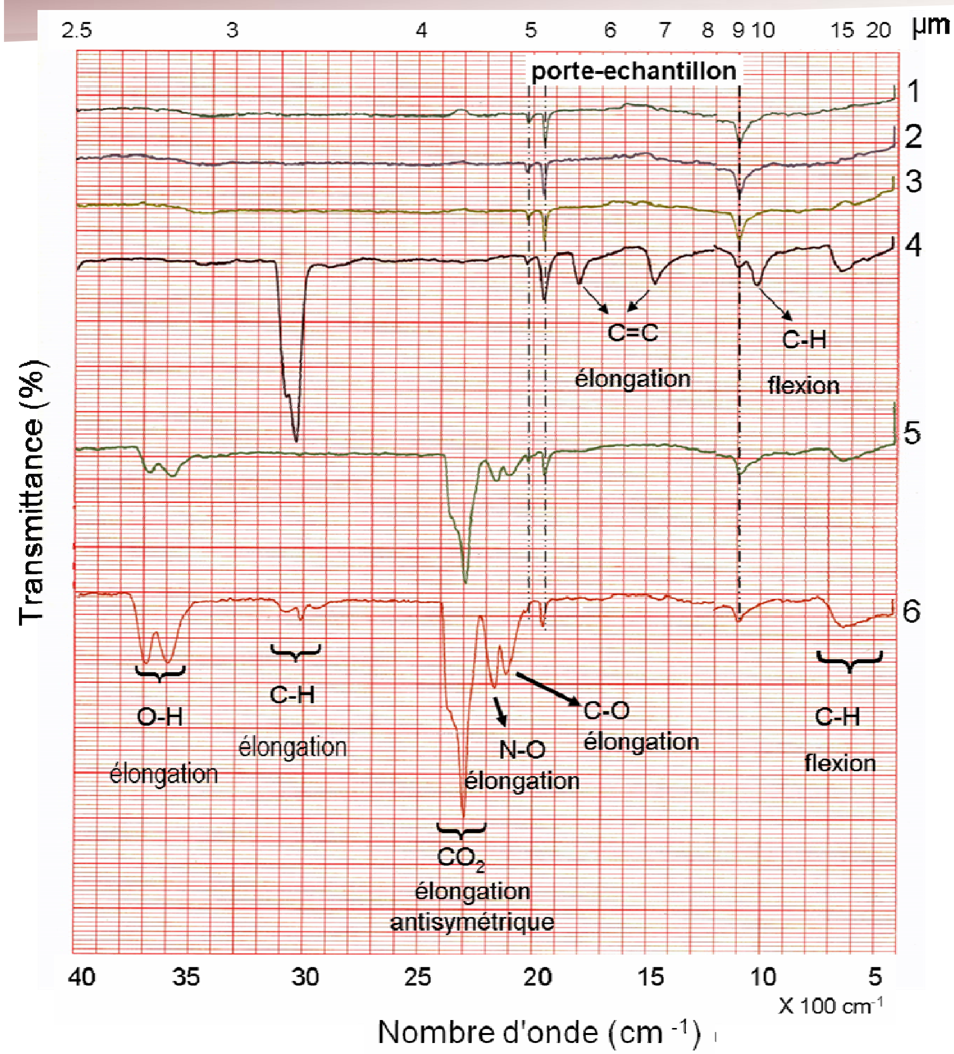


la présence du benzène sur la surface des poudres

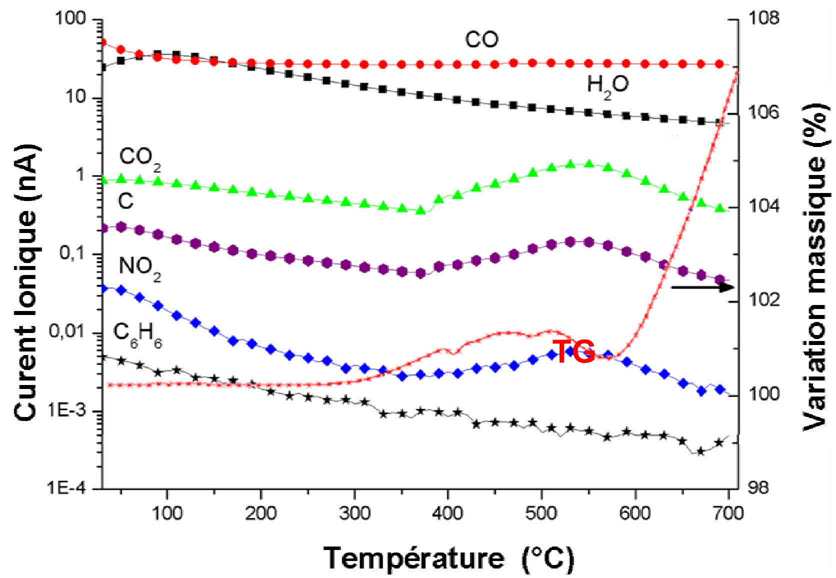
B. V. Neamţu, O. Isnard, I. Chicinaş, C. Vagner, N. Jumate, P. Plaindoux. Mater. Chem. Phys. 125 (2011) 364–369

Résultats et discussion – (i)

Investigation de la poudre par spectroscopies IR et SM-TG



Spectroscopie en infrarouge (IR)



Analyse de thermogravimétrie (TG) couplée avec la spectrométrie de masse (SM)

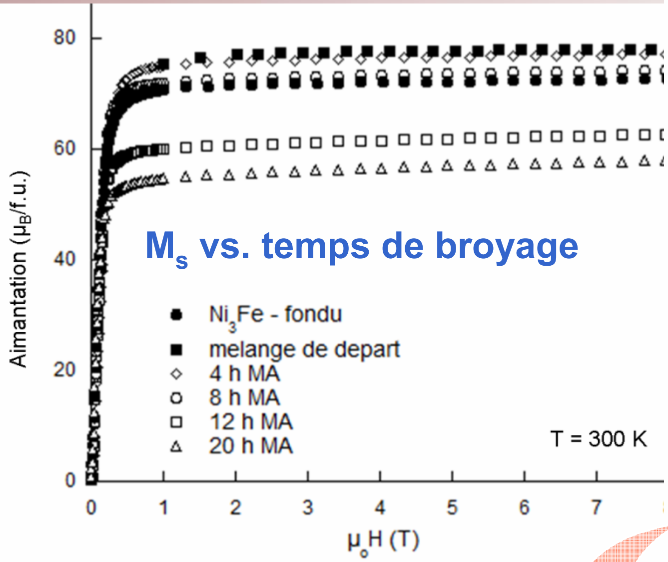
L'élimination et la décomposition du benzène pendant le recuit

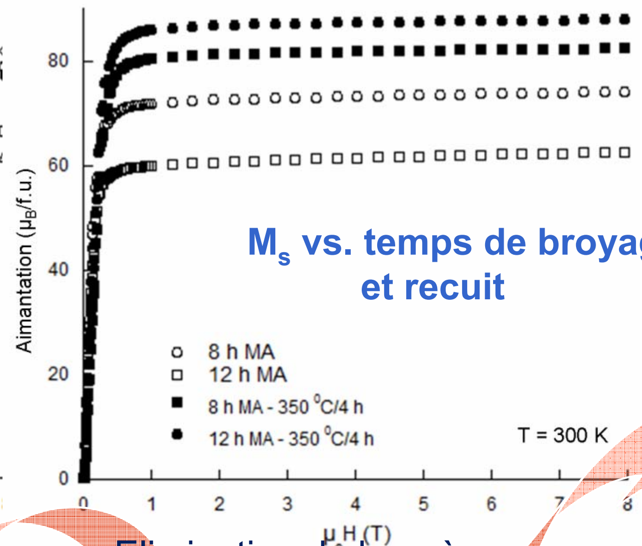
Ni, Fe, etc sont des catalyseurs pour la décomposition des hydrocarbures

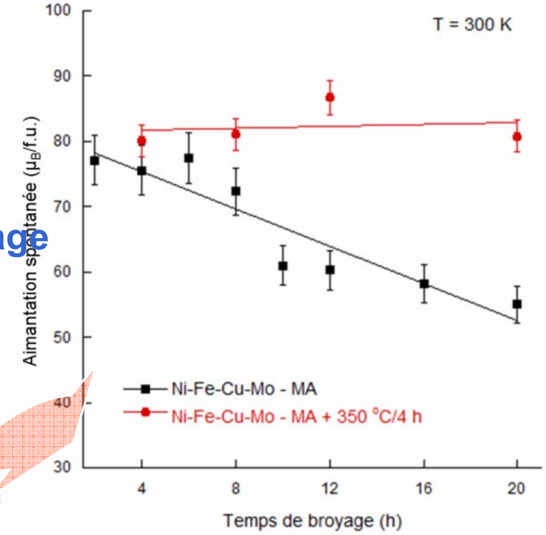
B. V. Neamţu, O. Isnard, I. Chicinaş, C. Vagner, N. Jumate, P. Plaindoux. Mater. Chem. Phys. 125 (2011) 364–369

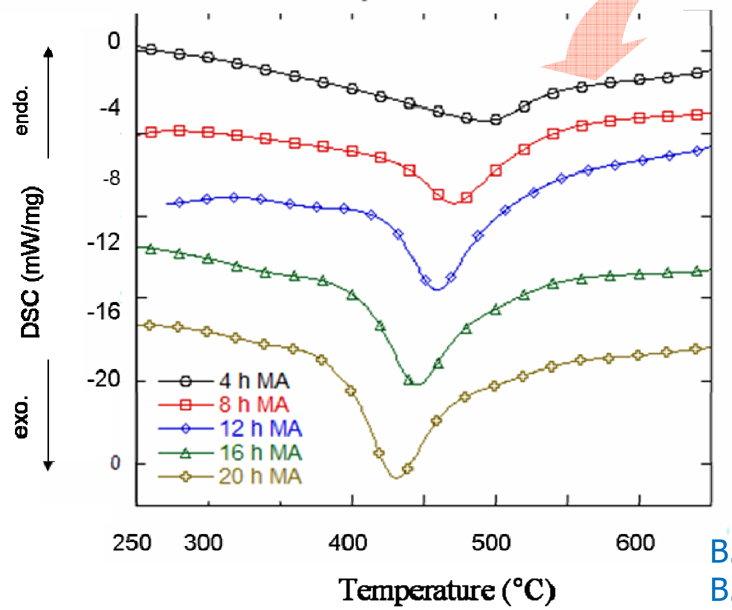
Résultats et discussion : (i) l'alliages de type Supermalloy

Propriétés magnétiques de la poudre









Elimination de benzène, Contraintes et défauts

↑

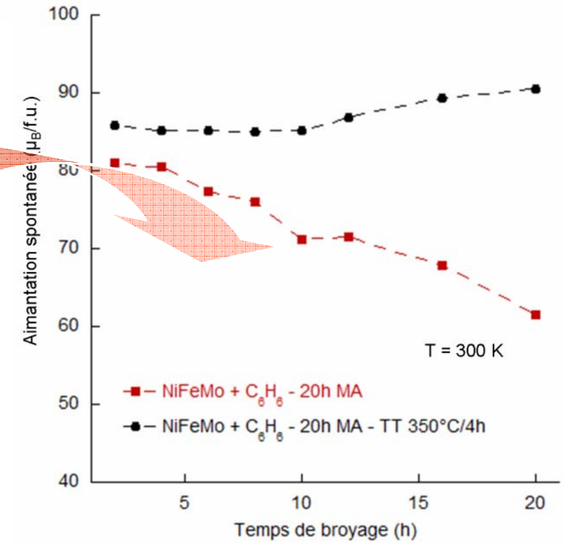
Recuit (350 °C/4h)

↑

Adsorption de benzène Contraintes et défauts

↑

Broyage mécanique par voie humide

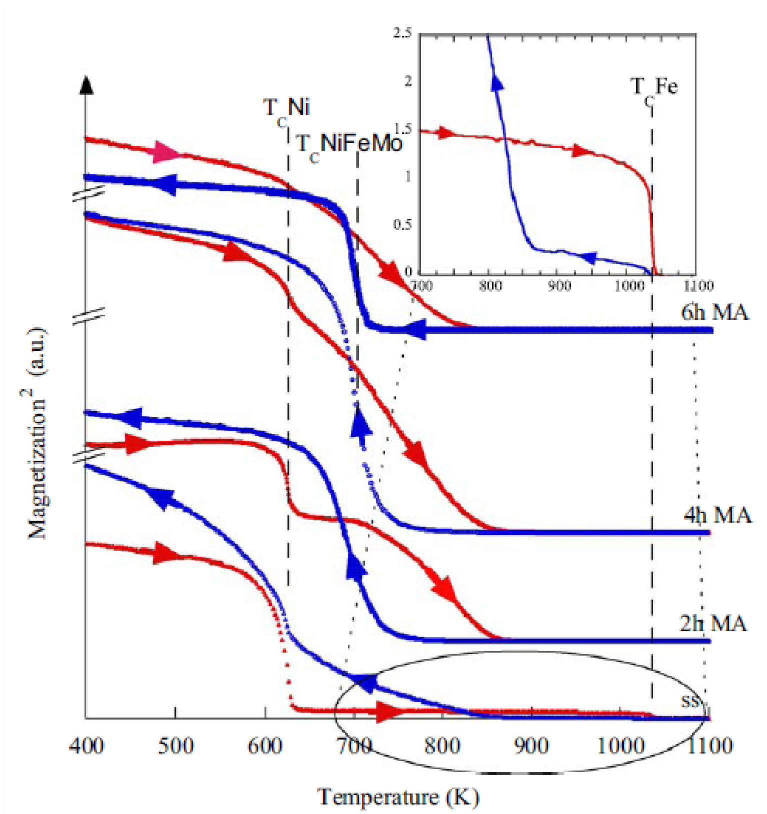


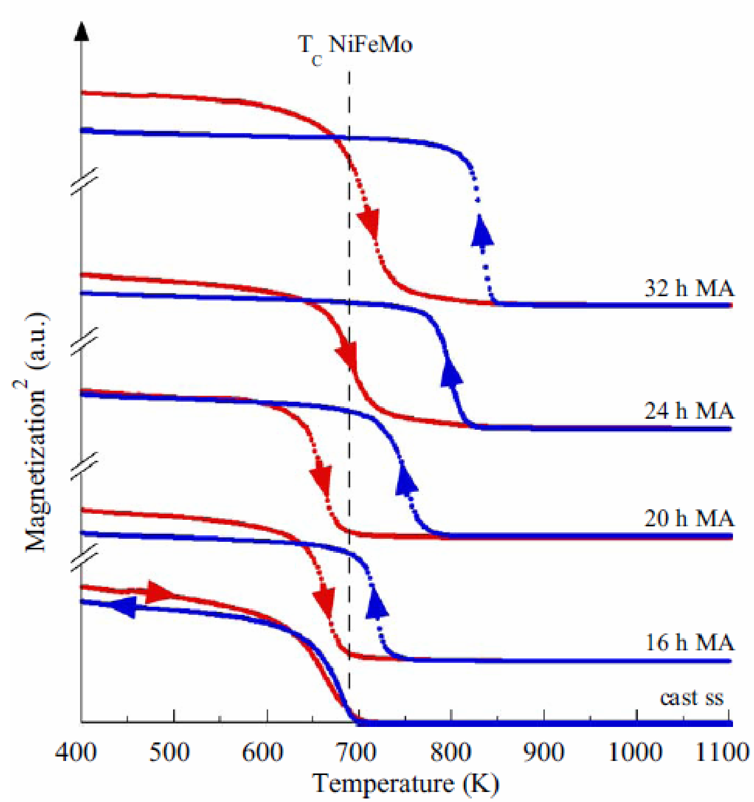
B.V. Neamţu, O. Isnard, I. Chicinaş, V. Pop, IEEE Trans. Magn. 46 (2010) 424-427

B.V. Neamţu, O. Isnard, I. Chicinaş, V. Pop, J. Alloys Comp. 509 (2011) 3632-3637

Résultats et discussion : (i) l'alliages de type Supermalloy

Thermomagnetic measurements

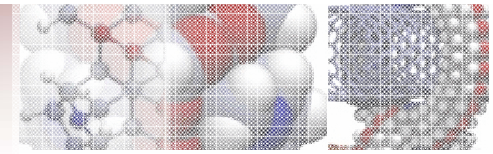




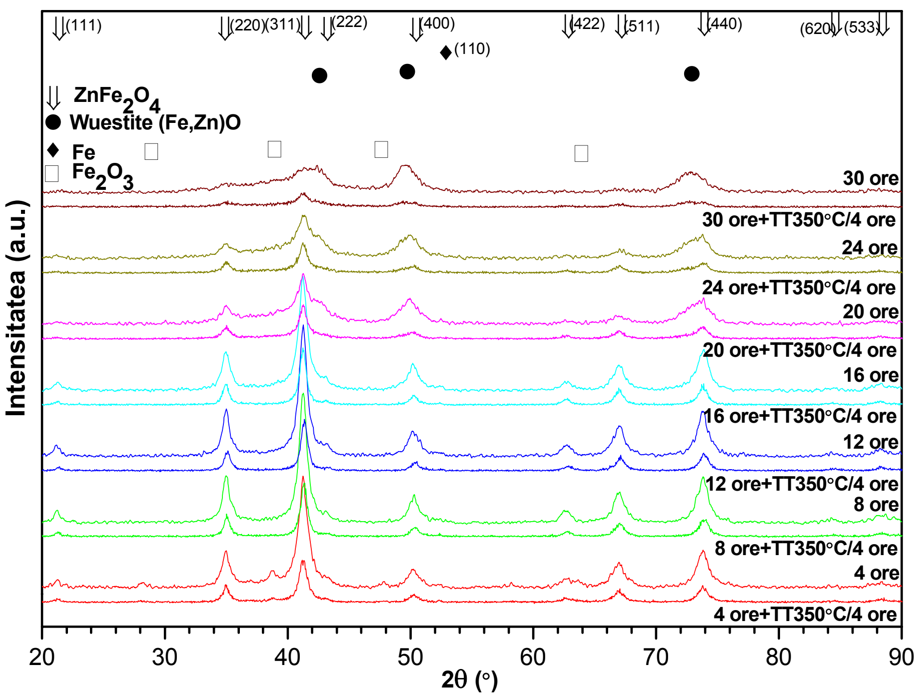
The difference between the Curie temperature recorded at heating and at cooling is a consequence of the powder contamination with iron during milling.

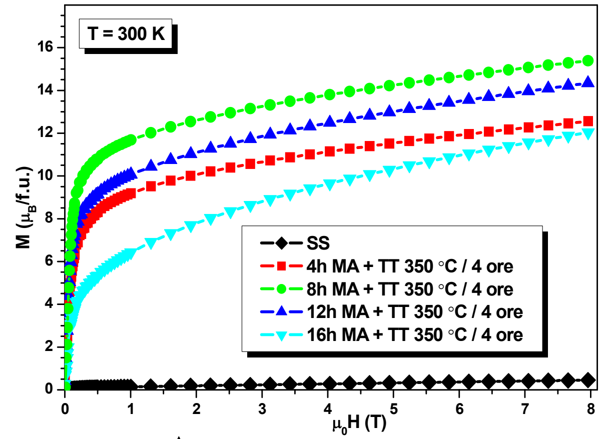
F. Popa, O. Isnard, I. Chicinaş, V. Pop, J. Magn. Magn. Mater. 322 (2010) 1548–1551

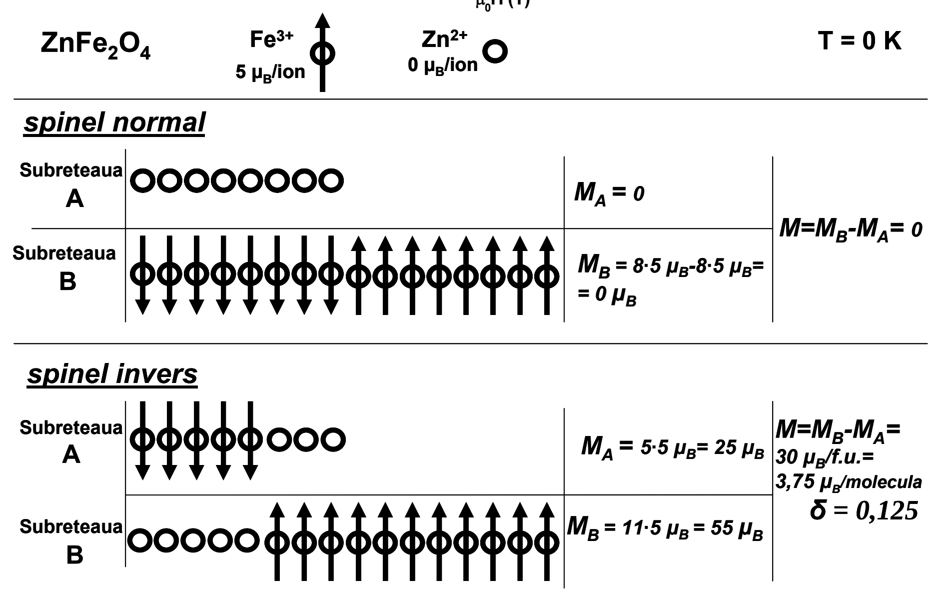
(ii) Soft magnetic nanocomposite powders like $MeFe_2O_4$/(Fe-Ni, Ni-Fe-X)



$ZnFe_2O_4$, $NiFe_2O_4$ and $CuFe_2O_4$ ferrites have been obtained by reactive milling







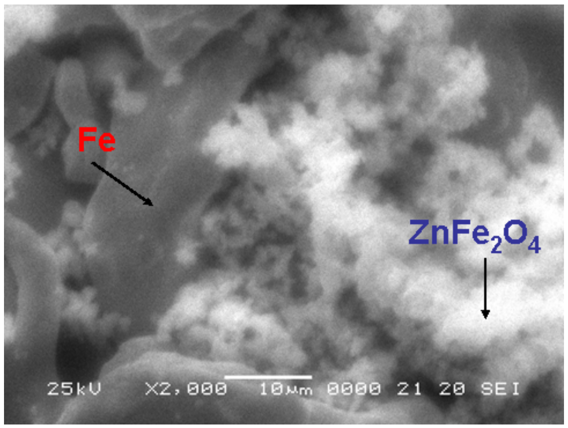
T.F. Marinca, I. Chicinaş, O. Isnard, V. Pop, Optoelectron Adv. Mater. – Rapid Commun. 5 (2011), 39-43

T.F. Marinca, I. Chicinaş, O. Isnard, V. Pop, F. Popa, J. Alloys Compd. DOI: 10.1016/j.jallcom.2011.05.040 (2011)

(ii) Soft magnetic nanocomposite powders like $MeFe_2O_4$/(Fe-Ni, Ni-Fe-X)

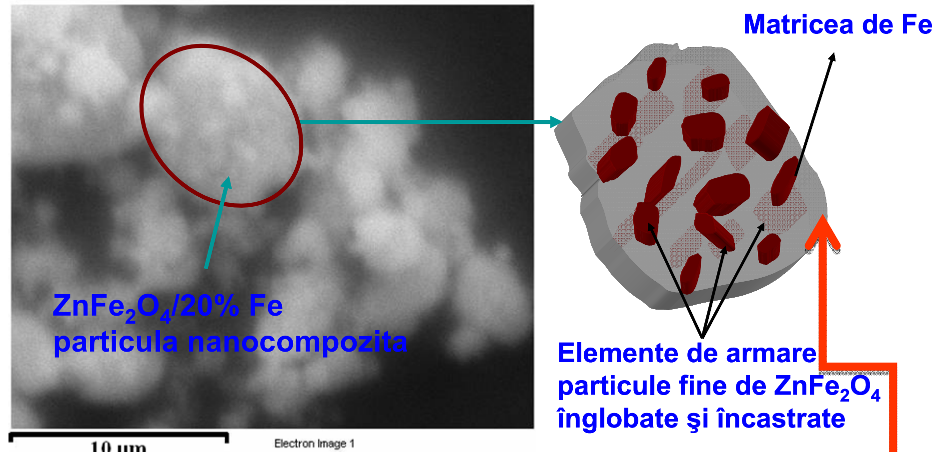
Producing of nanocomposite particles by milling

Nano $ZnFe_2O_4$/(20, 30, 50) wt% Fe mixture

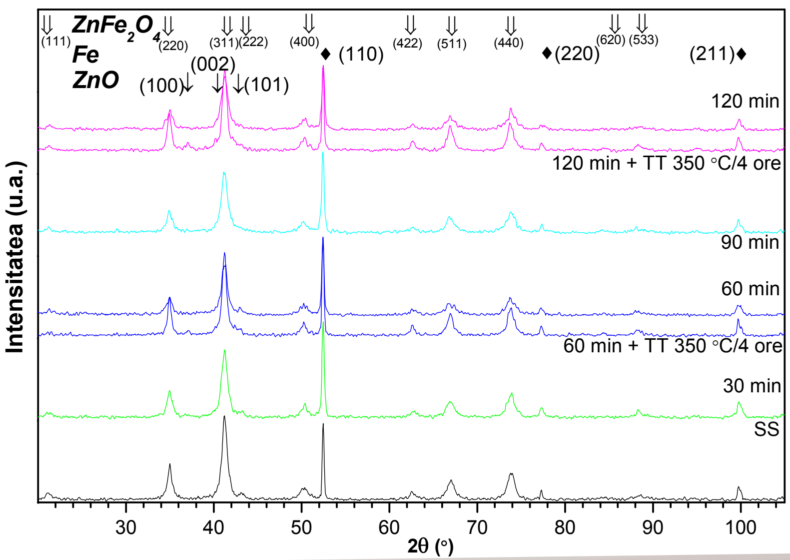


120 min milling

$ZnFe_2O_4$/20 wt% Fe nanocomposite particles



Particle similar to the “raisin-bread” model

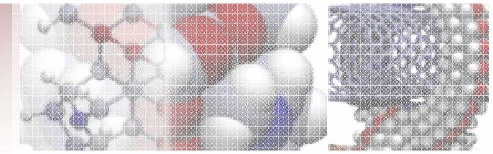


By milling the initial phases are conserved

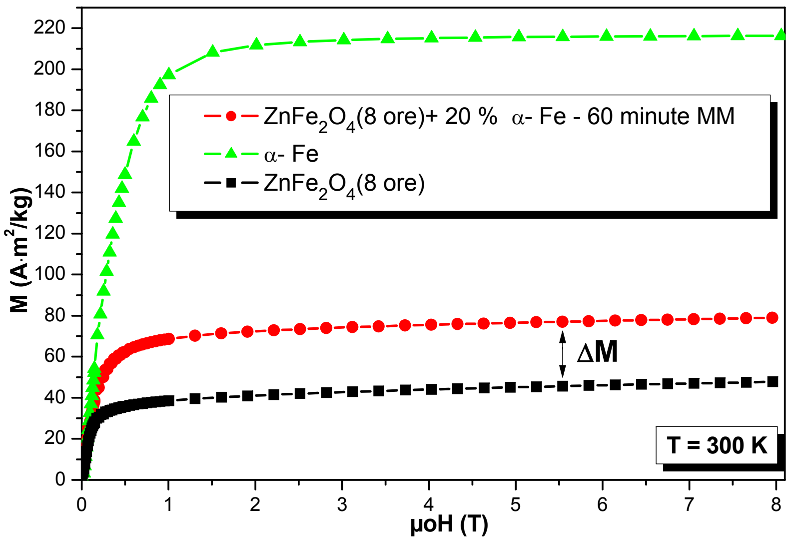
Milling ++ annealing

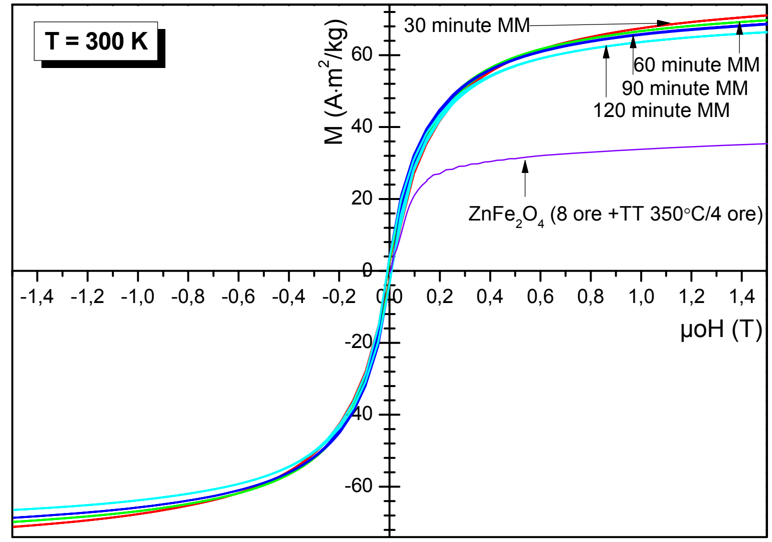
$$ZnFe_2O_4 \rightarrow \lambda \cdot ZnO + Zn_{1-\lambda}Fe_2O_{4-\lambda} \Rightarrow Zn_{0,55}Fe_2O_{3,55}$$

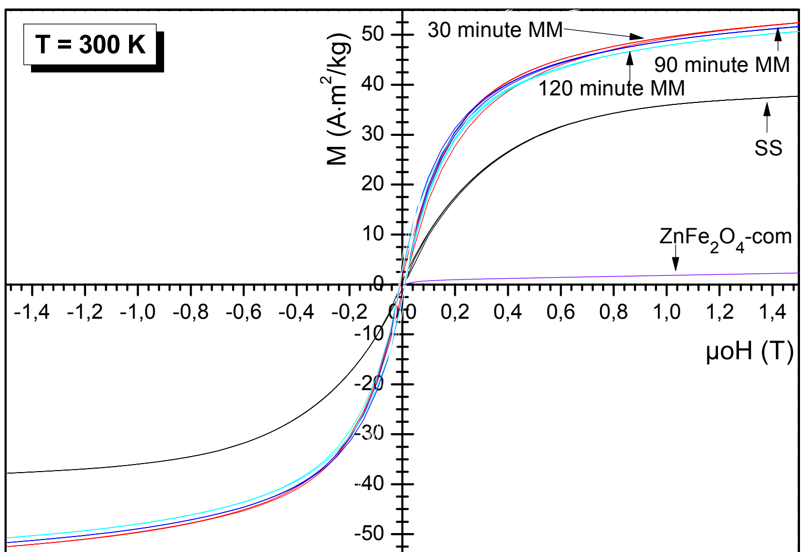
(ii) Soft magnetic nanocomposite powders like $MeFe_2O_4$/(Fe-Ni, Ni-Fe-X)

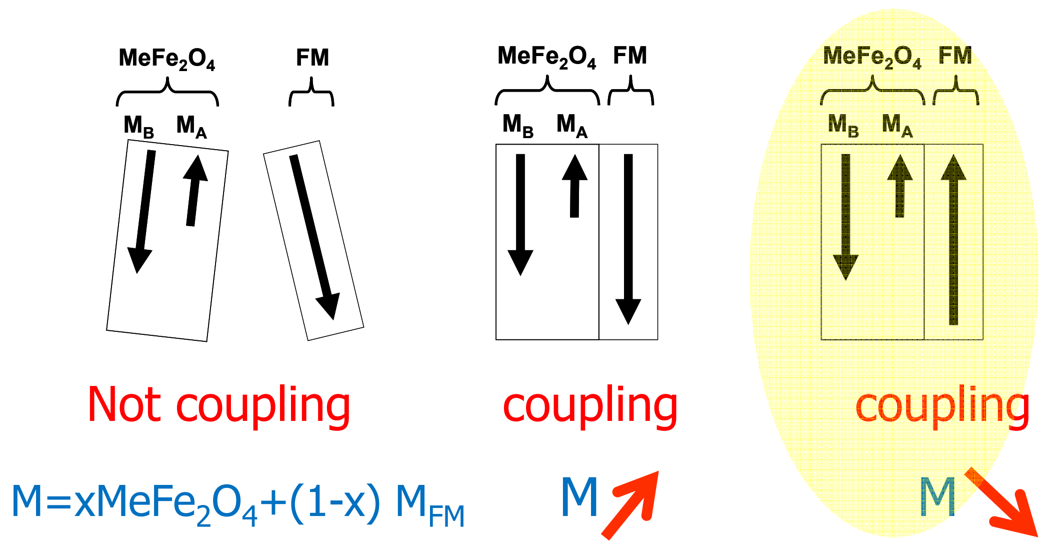


Magnetic properties



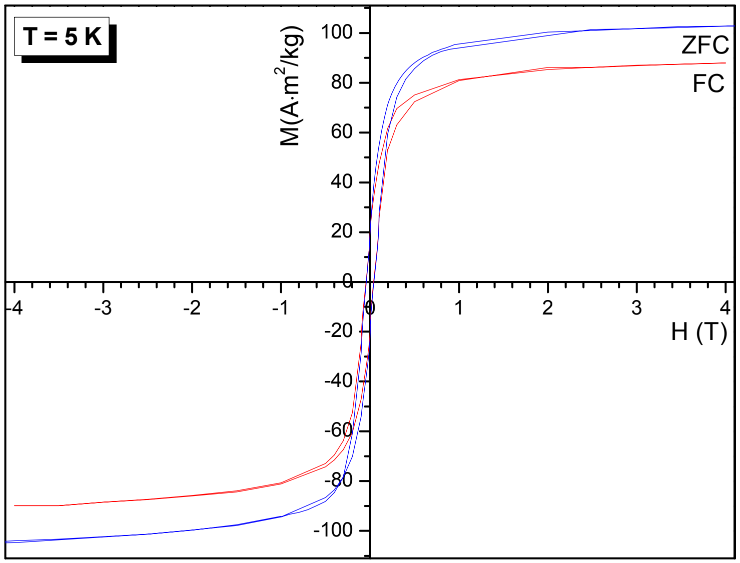


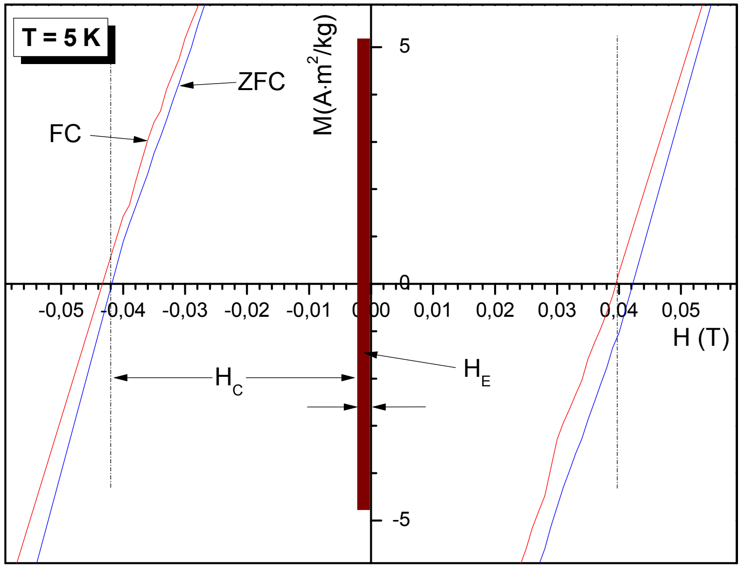




(ii) Soft magnetic nanocomposite powders like $MeFe_2O_4$/(Fe-Ni, Ni-Fe-X)

Cuplajul magnetic – Exchange bias



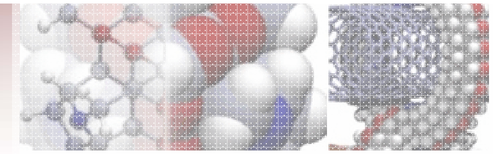


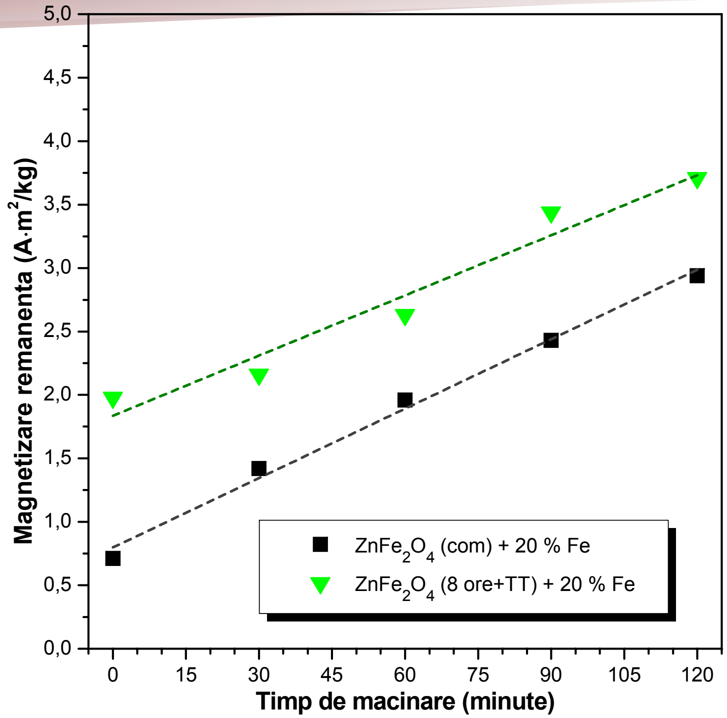
Exchange-bias field

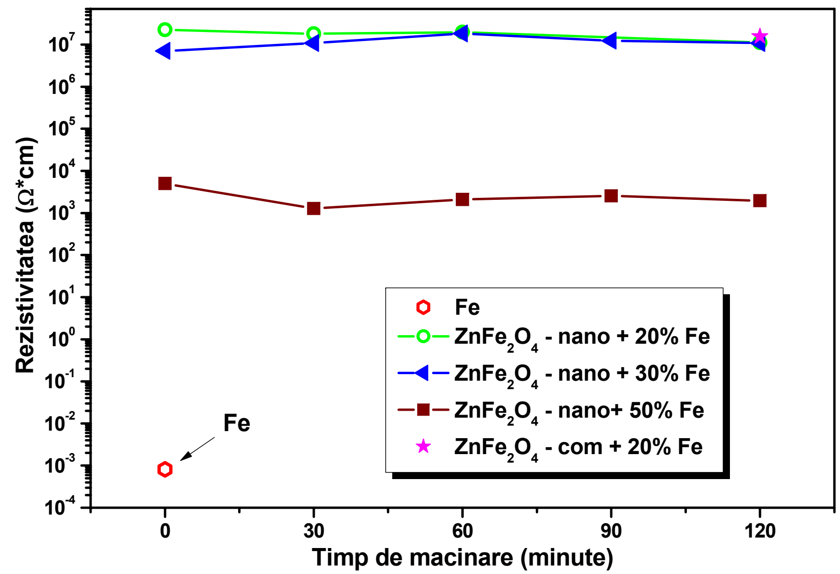
$$H_E = \left(H_{C-left} - H_{C-right}\right)/2$$

H_E = 2 mT.

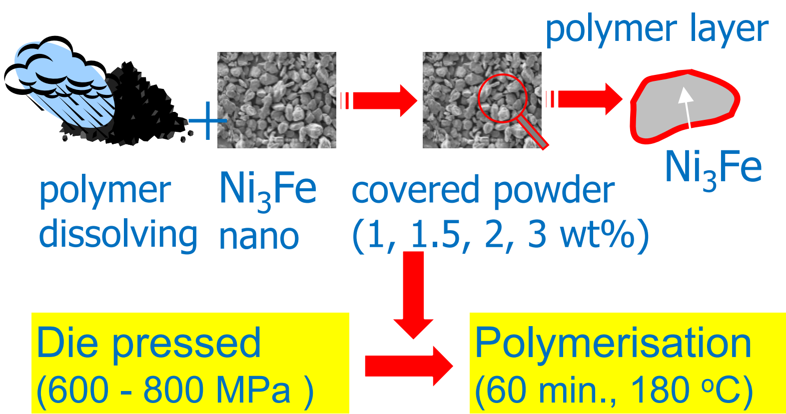
(ii) Soft magnetic nanocomposite powders like $MeFe_2O_4$/(Fe-Ni, Ni-Fe-X)

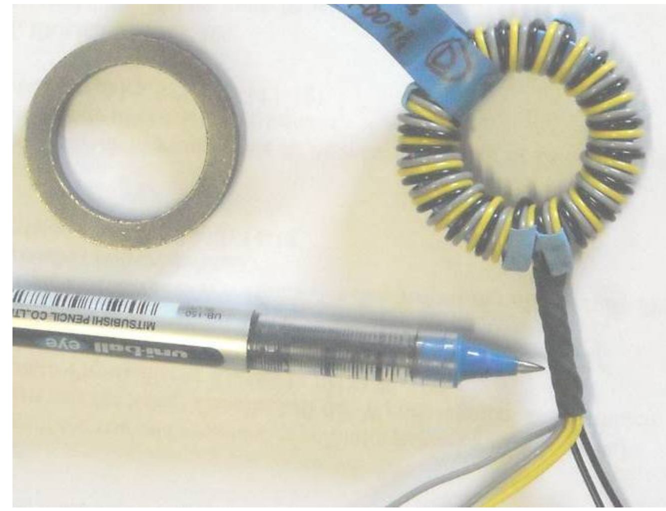






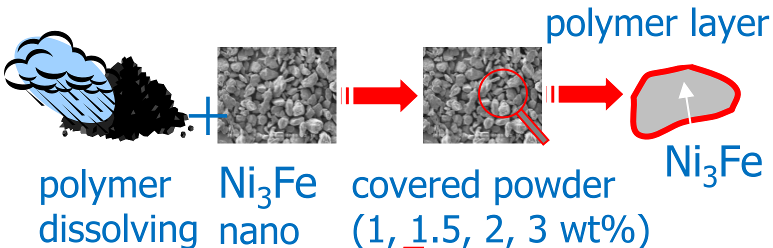
A. Soft magnetic composites (SMC)



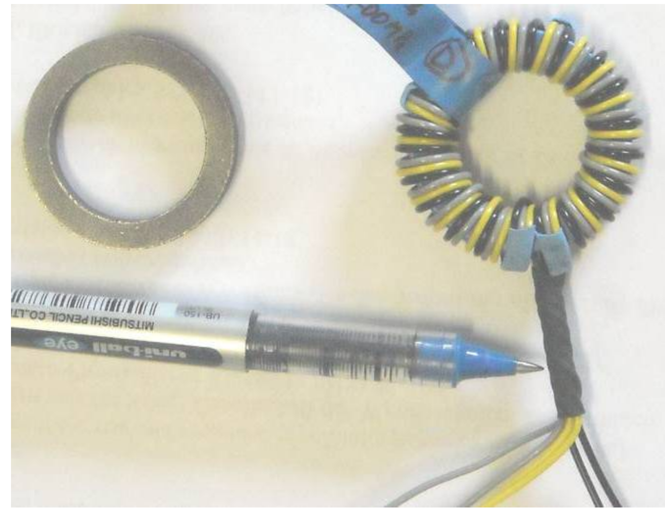


(iii) Soft magnetic nanocrystalline/nanocomposites compacts

A. Soft magnetic composites (SMC)

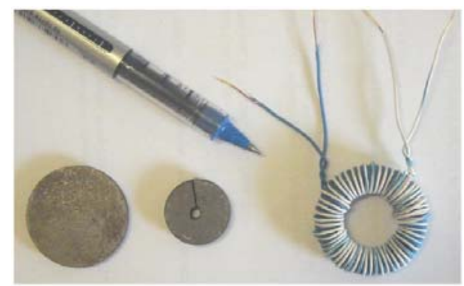


Die pressed (600 - 800 MPa) → **Polymerisation** (60 min., 180 °C)

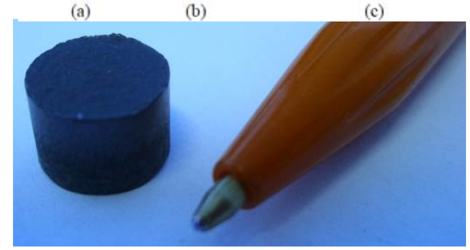


B. Spark plasma sintering

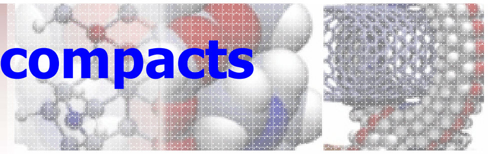
Home-made SPS equipment (Tech.univ. Cluj-Napoca)



(a) (b) (c)



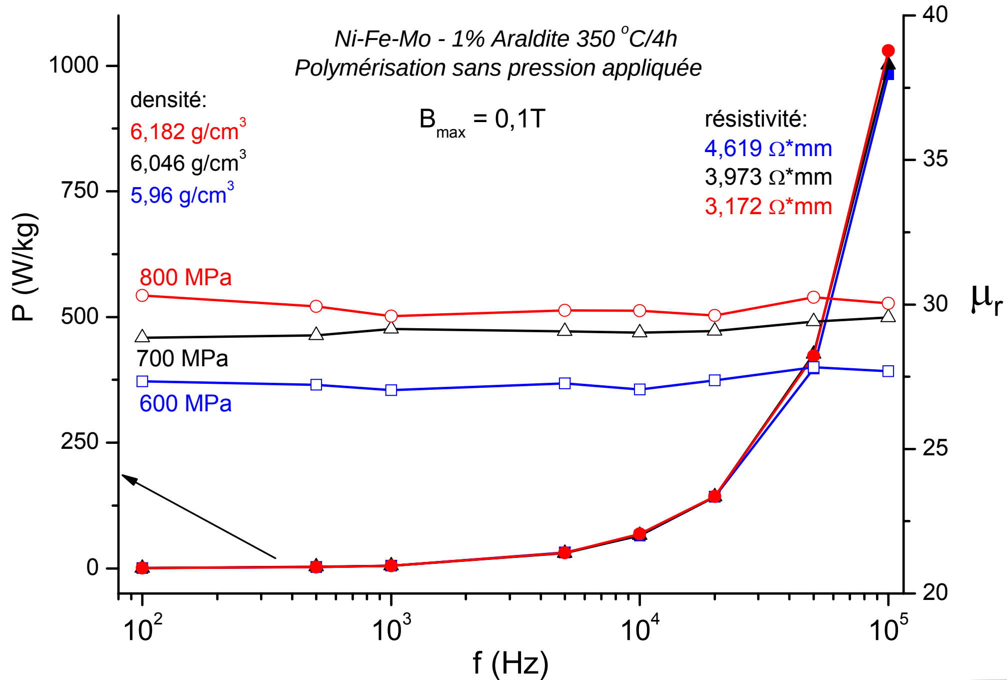
(iii) Soft magnetic nanocrystalline/nanocomposites compacts



Some results:

A. Soft magnetic composites (SMC)

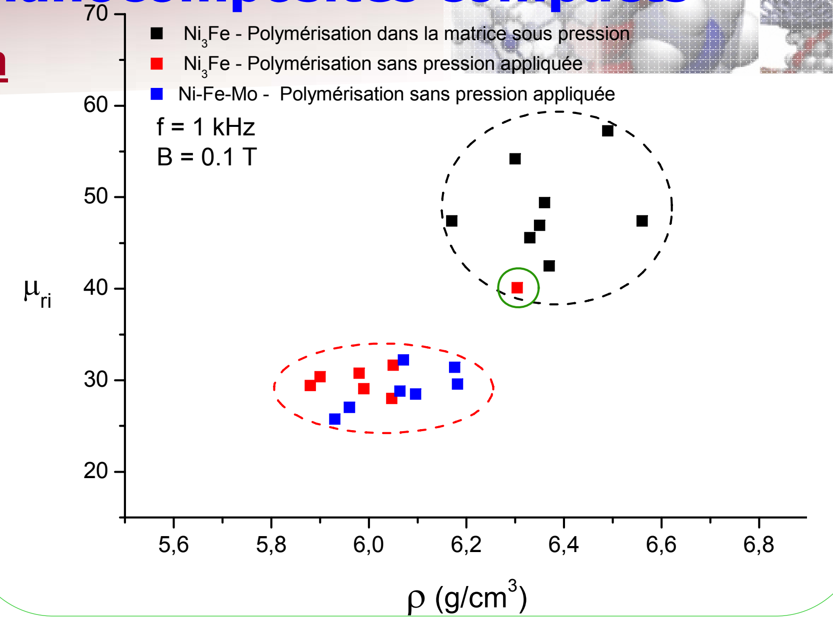
Two type of nanocrystalline powders were used: Ni3Fe, Supermalloy
- different compaction pressures
- two methods of polymerization
- different dielectric content, with/whitout lubricant/silane
- heat treatment post-polymerization
- DC/AC characterisation



(iii) Soft magnetic nanocrystalline/nanocomposites compacts

Some results: **Imagine de ansamblu asupra caracteristicilor compactelor**

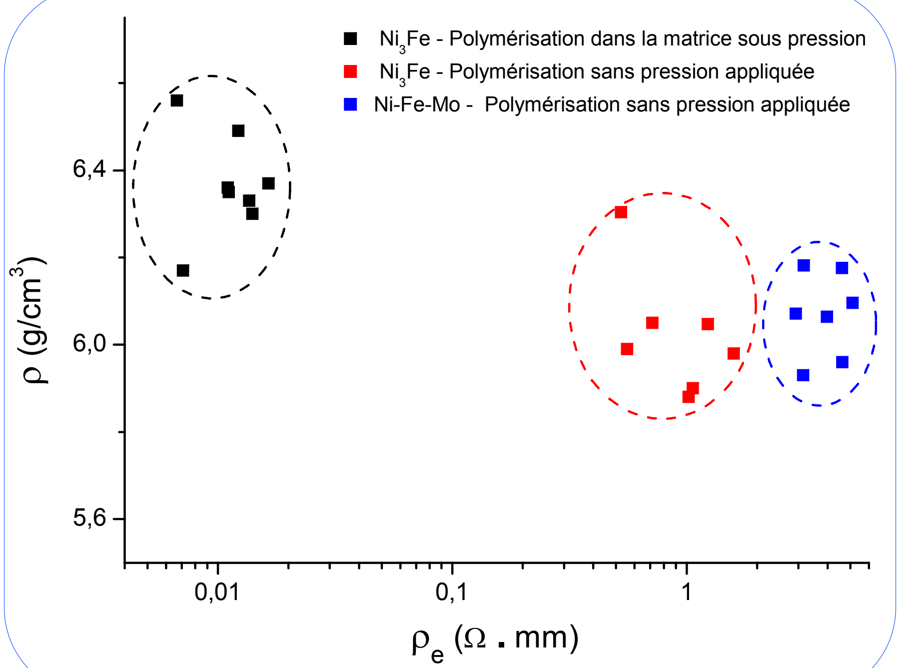
$\mu_{ri} = f(\rho)$ → două familii de puncte
(metoda de polimerizare)

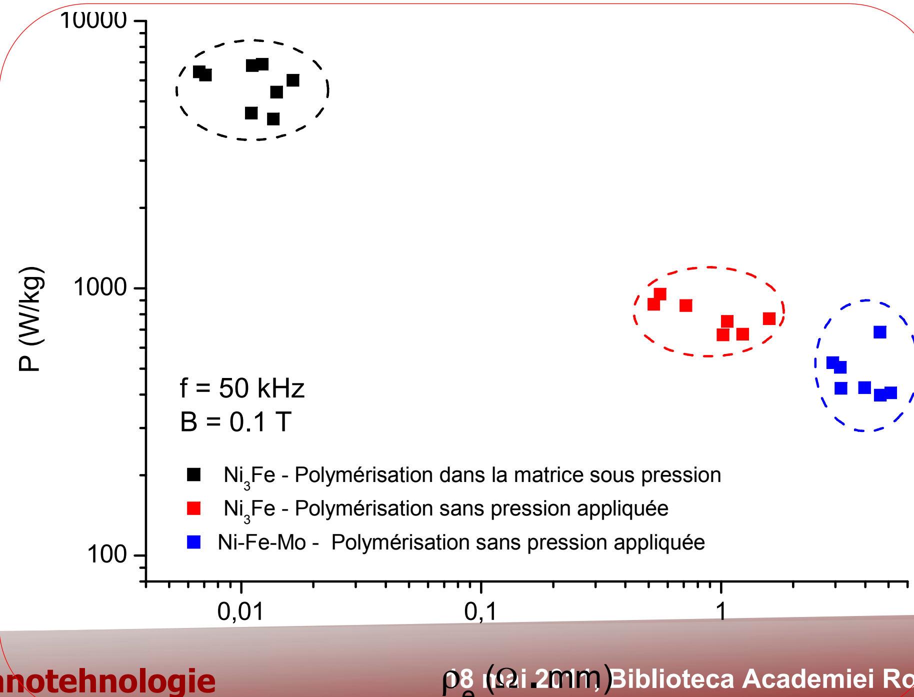


$\rho = f(\rho_e)$

$P = f(\rho_e)$

Trei familii de puncte
(metoda de polimerizare şi rezistivitatea intrinsecă (NiFeMo))

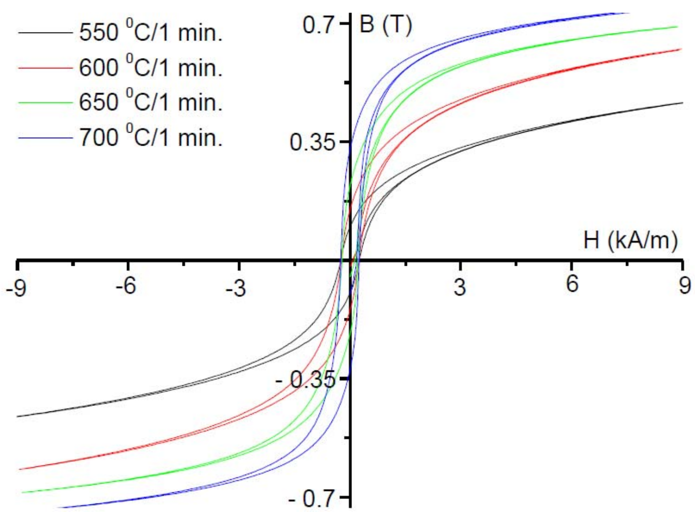


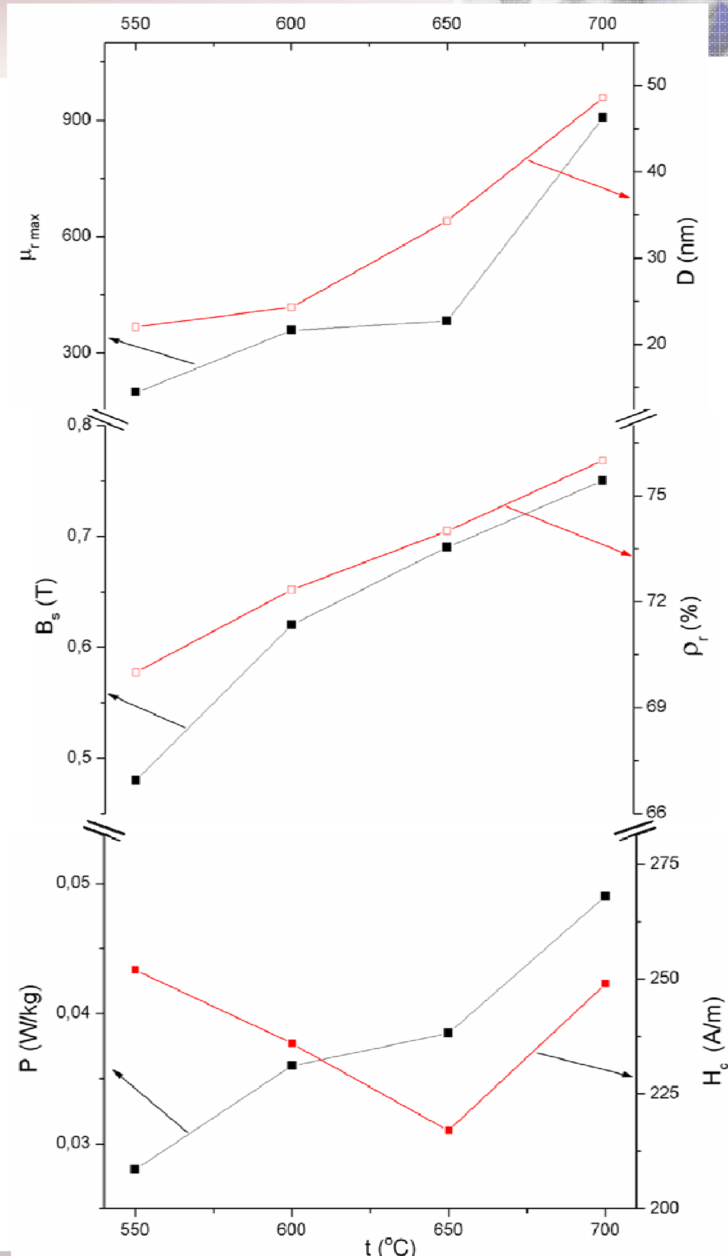


(iV) Soft magnetic nanocrystalline/nanocomposites compacts

Some results:

B. Spark plasma sintered compacts

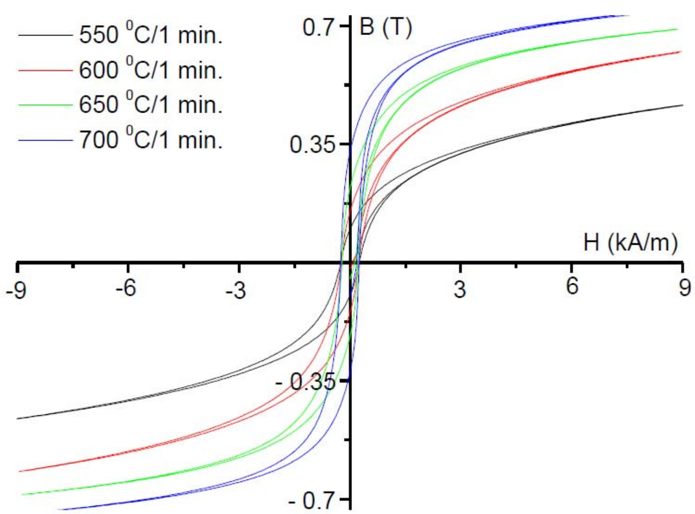


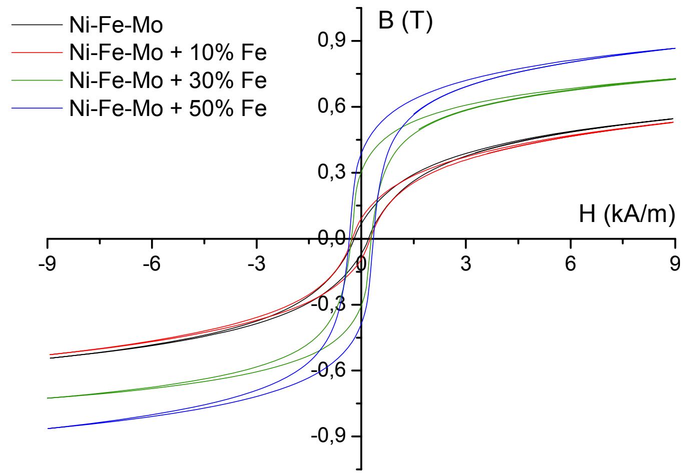


(iV) Soft magnetic nanocrystalline/nanocomposites compacts

Some results:

B. Nanocrystalline sintered compacts obtained by SPS



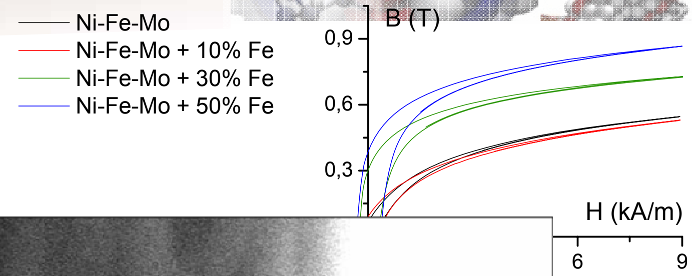


Magnetic characteristics of Ni-Fe-Mo + (X%) Fe sintered compacts (X = 0 … 50 wt.%). Sintering parameters: 600 °C/2 min./30 MPa

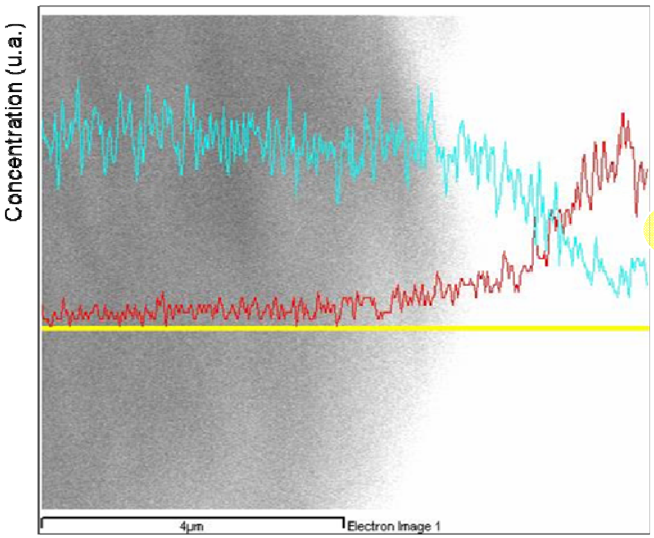
	Relative density (%)	$\mu_{r\,max}$	B_s (T)	H_c (A/m)	B_r (T)	ρ µΩ·mm
79Ni16Fe5Mo	72,5	188	0,55	205	0,07	124,35
79Ni16Fe5Mo + 10 % Fe	74	186	0,53	256	0,09	134,17
79Ni16Fe5Mo + 30 % Fe	81,9	452	0,73	283	0,30	160,30
79Ni16Fe5Mo + 50 % Fe	81,5	457	0,87	345	0,39	164,62

(iV) Soft magnetic nanocrystalline/nanocomposites compacts

Some results:

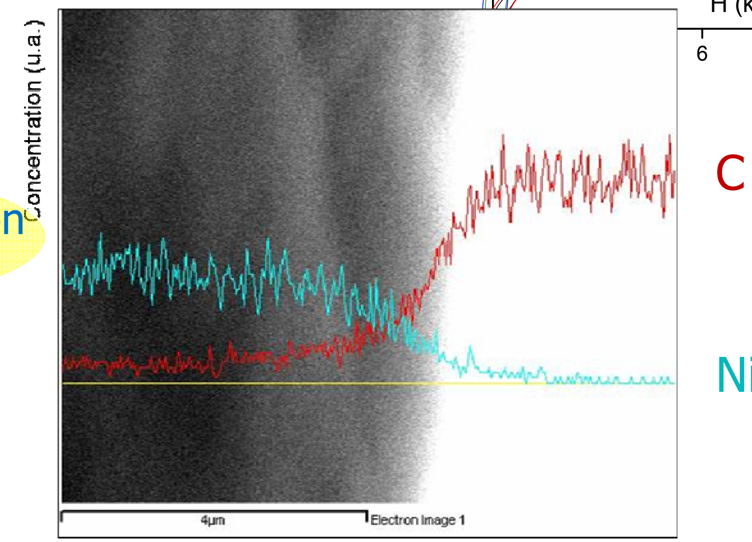


B. Nanocrystalline sintered compacts obtained by SPS



Ni_3Fe – SPS - 650 °C/1 min.

Carbon contamination from graphite die



Ni_3Fe – SPS - 700 °C/1 min.

An annealing in H_2, **450 °C/4 h**

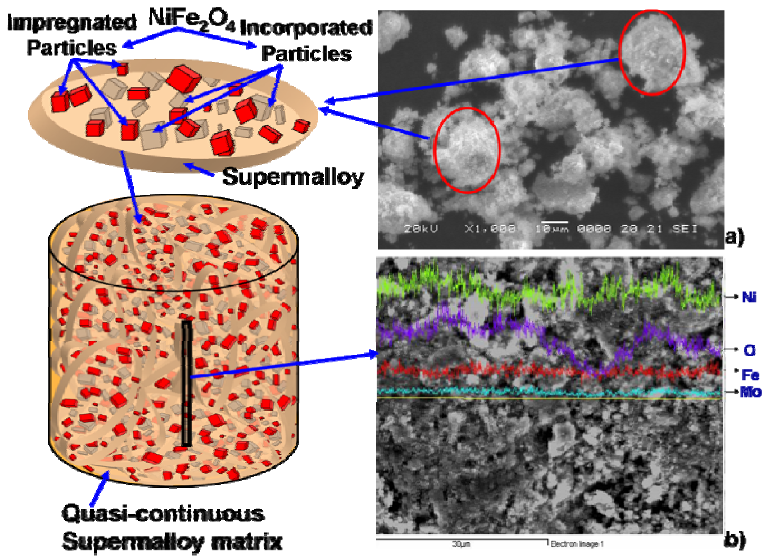
Coercive field decreases by 50%
Permeability increases by 600%

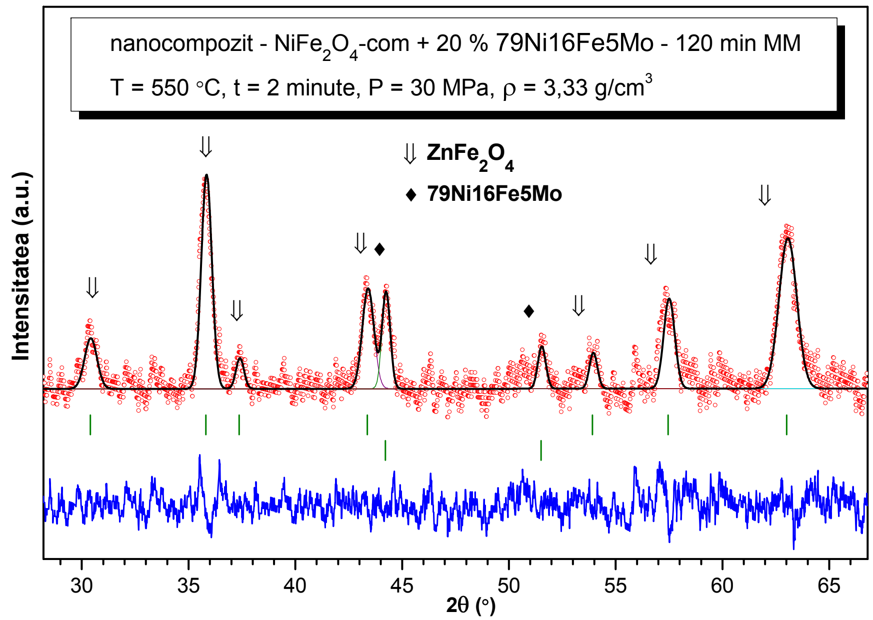
(iV) Soft magnetic nanocrystalline/nanocomposites compacts

Some results:

B. Nanocomposite sintered compacts obtained by SPS: $ZnFe_2O_4$/(Fe,Ni), $NiFe_2O_4$/Supermalloy

Preliminary results





Electrical resistivity:

Sintered nanocomposite: $\rho_e=9.5\cdot10^3\ \Omega\cdot cm$

Supermalloy: $\rho_e\sim 5.7\cdot10^{-7}\ \Omega\cdot cm$

Ni-ferrite: $\rho_e=10^6\div10^9\ \Omega\cdot cm$

Conclusions

We have developed a protocol (method + parameters) : wet/dry mechanical alloying followed by an annealing at low temperature for producing of nanocrystalline sot magnetic powders.

Magnetisation decreases by increasing milling time. An annealing at 350 °C, 4 hours increases the magnetisation.

The influence of benzene on the magnetisation have been determined. The removing of benzene by annealing elucidated by a combination of methods: DSC, IR, SM-TG.

Nanocomposite powders lie $MeFe_2O_4$/(Fe, Ni, Fe-Ni alloy) obtained by mechanical milling realizes a compromise between alloy magnetization and electrical resistivity of ferrites

Soft magnetic nanocrystalline compacts obtained by mechanically alloyed powders and dielectric can be used as magnetic cores at frequencies higher than 100 kHz

SPS is a suitable method to obtain nanocomposite sintered compacts

Aknowledgements:

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Eugen Dorolti, Viorel Pop

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At Babe

Thank you for your attention!

Multumesc!

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