SOFT MAGNETIC NANOCRYSTALLINE/NANOSTRUCTURED MATERIALS PRODUCED BY MECHANICAL ALLOYING ROUTES

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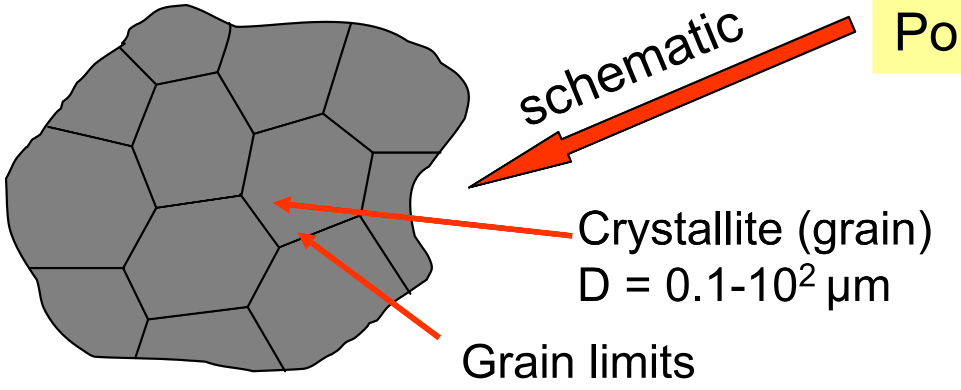
Technical University of Cluj-Napoca, Romania

What are Nanocrystalline Materials ?

Polycrystalline materials



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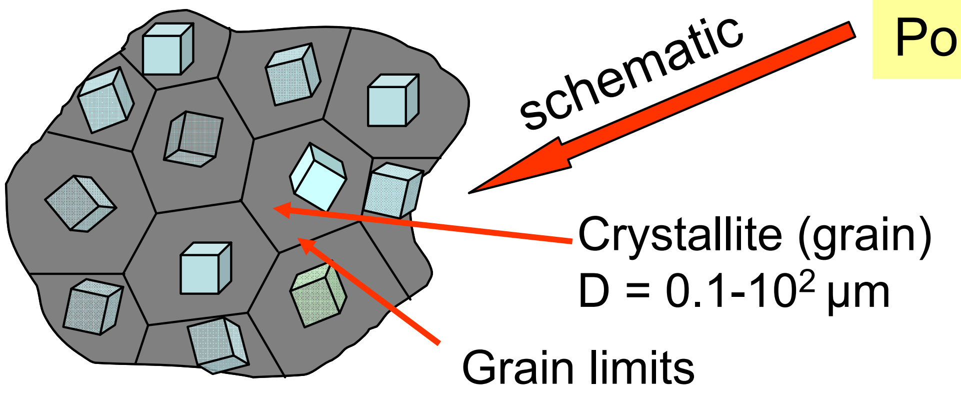

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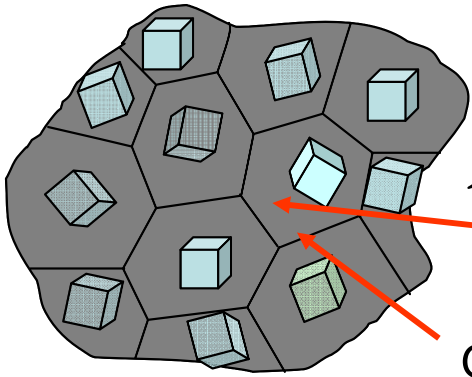
Polycrystalline materials

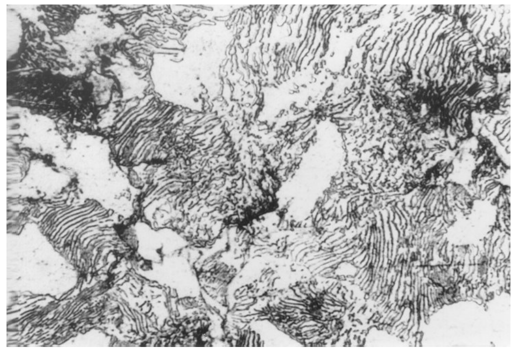
schematic

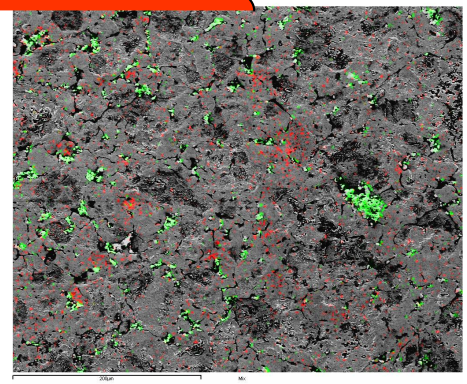


Crystallite (grain)
D = 0.1-10^2 μm

Grain limits

Real images





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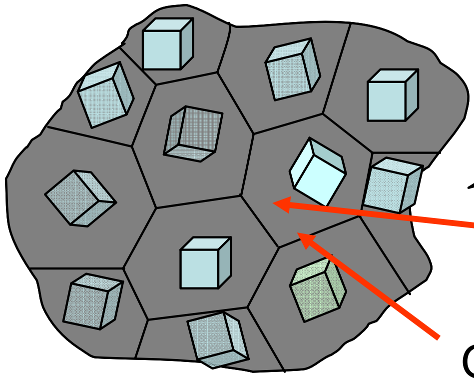

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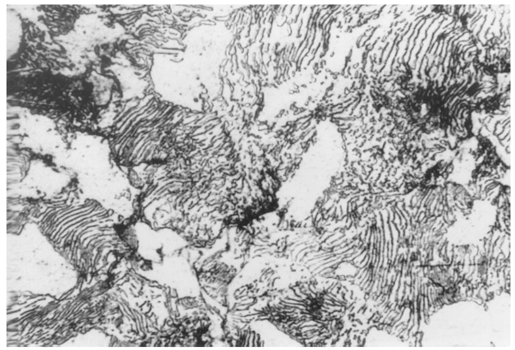

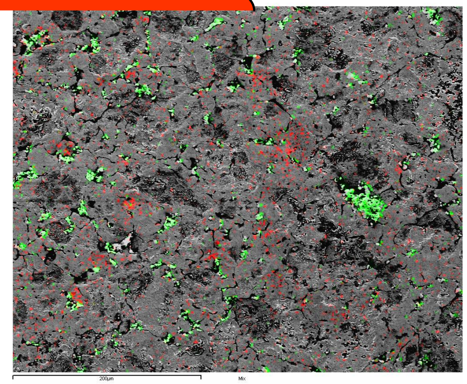

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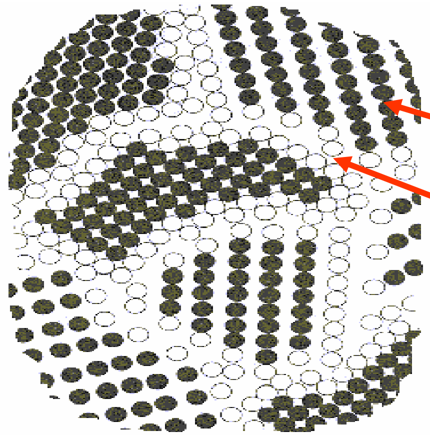

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● Atoms in grains

○ Atoms in limits

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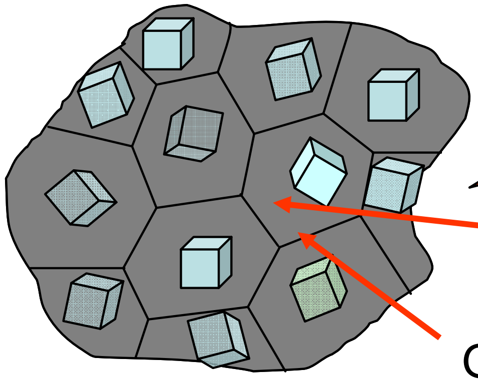

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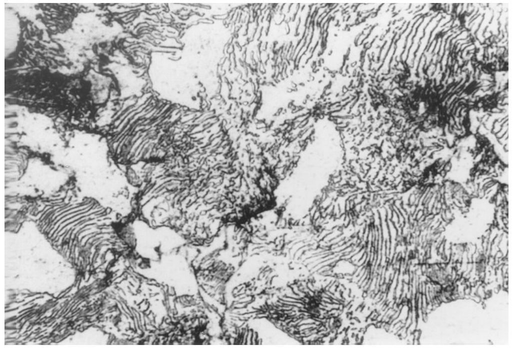

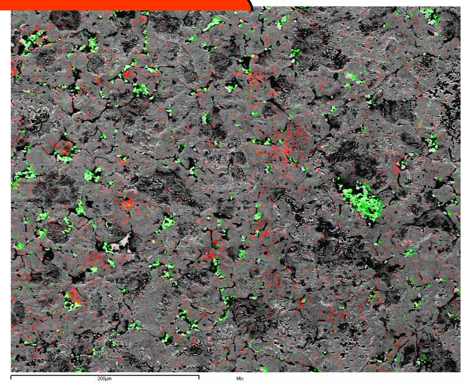

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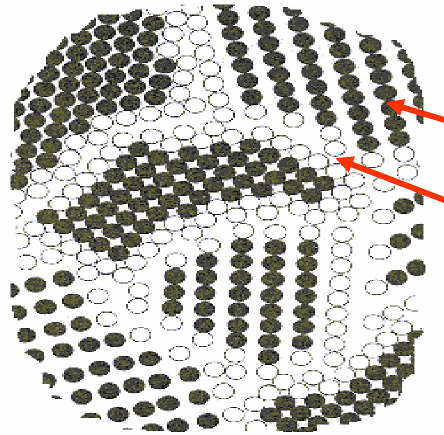

Crystallite (grain)
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● Atoms in grains

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Fraction of atoms in limits

$$F = \frac{3\Delta}{D}$$

Δ → Grain limit thickness

D → Crystallite size

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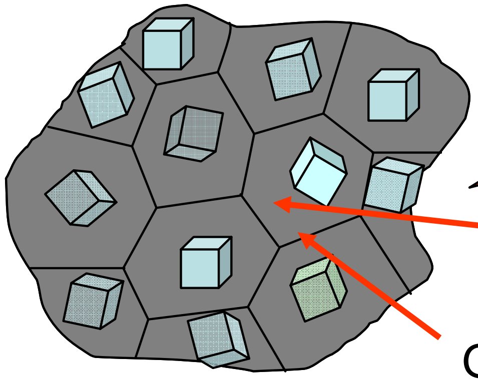

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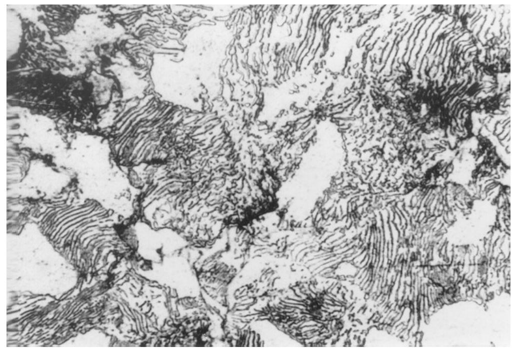

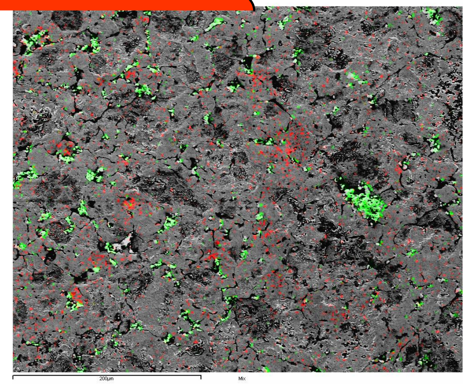

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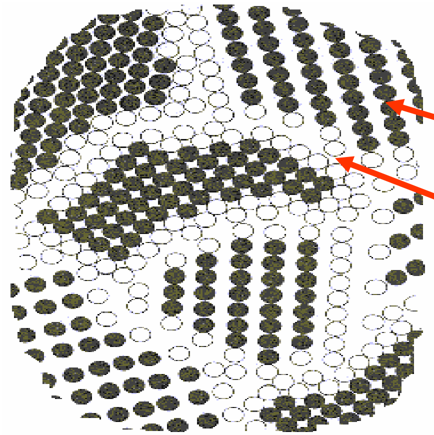

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$$F = \frac{3\,\Delta}{D}$$

Grain limit thickness

Crystallite size

Examples:

D = 5 nm → F = 50%

D = 10 nm → F = 30%

D = 100 nm → F = 3%

Why are important Nanocrystalline Materials ?
What really means the Nanocrystalline Materials ?
When a Material is really Nano?

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When a Material is Nano?

For example: Coercive field H_C

depend on

intrinsic properties (anisotropy)

structure (grain size, stresses, inclusions,etc.

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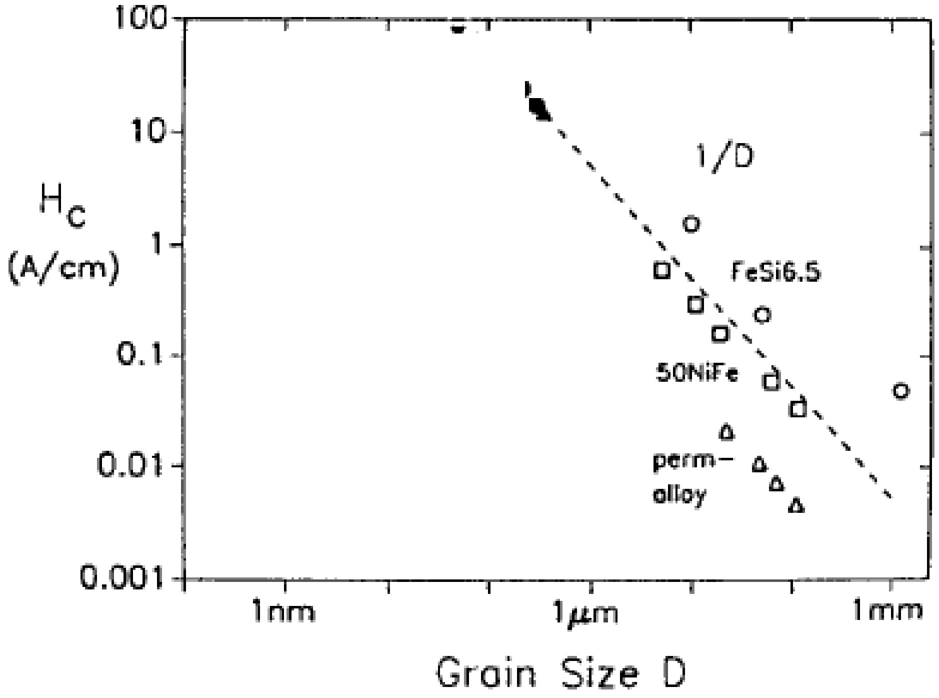

Polycrystalline materials

H_C ↗ when D ↘ and

$H_C \sim 1/D$

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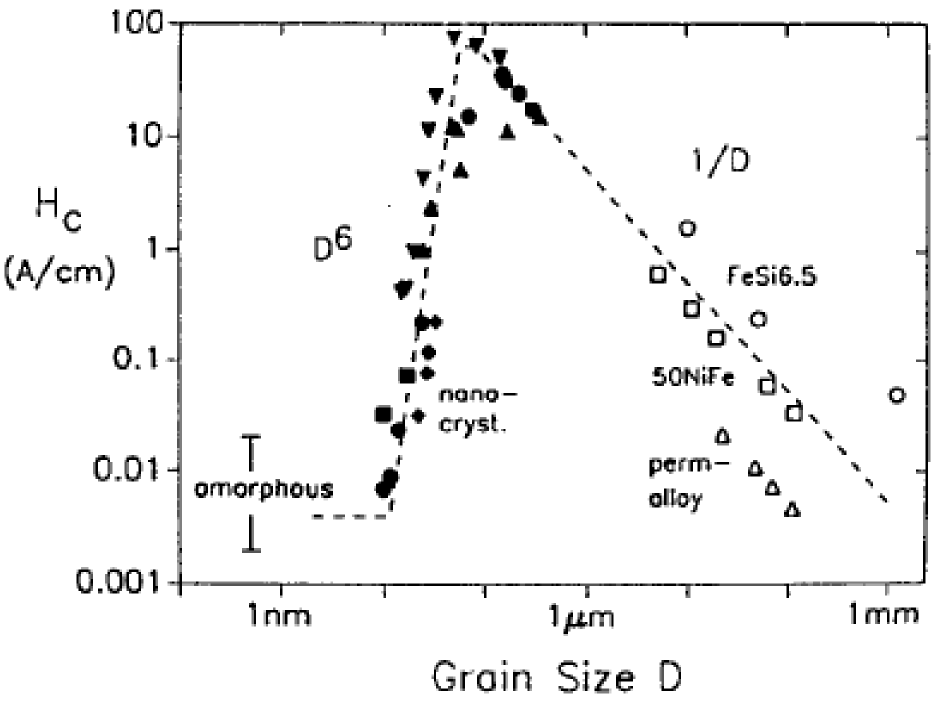

G. Herzer, Scripta Metall et Mater., 33 (1995) 1741-1756.

Polycrystalline materials

H_C ↗ when D ↘ and $H_C \sim 1/D$

Nanocrystalline materials

H_C ↘↘↘↘↘ when D ↘ and $H_C \sim D^6$

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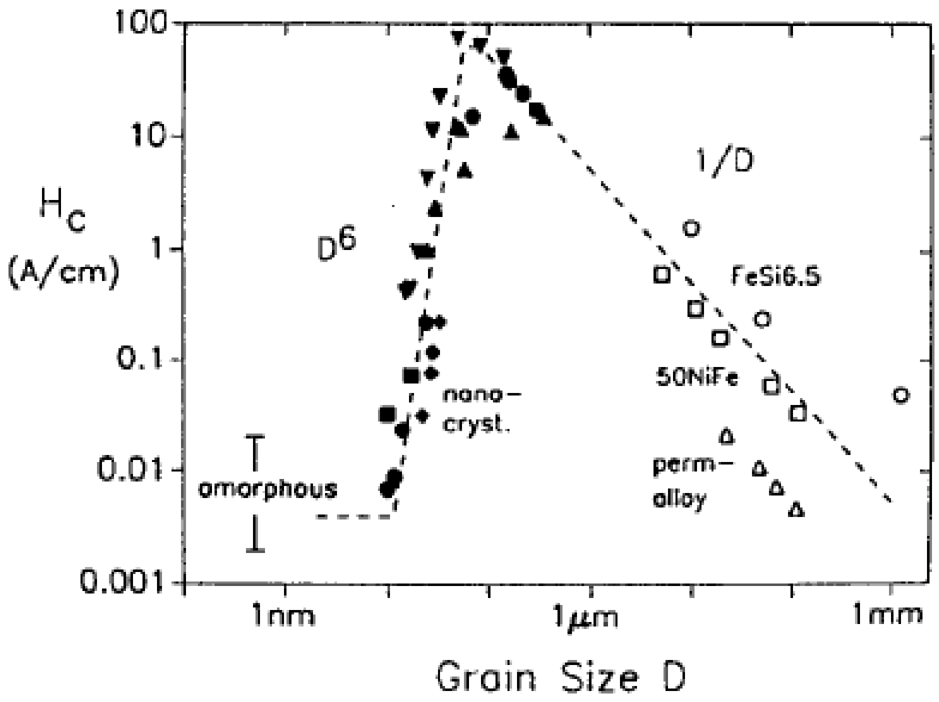

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Polycrystalline materials

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Nanocrystalline materials

$H_C \searrow\searrow\searrow\searrow\searrow$ when D $\searrow$ and $H_C \sim D^6$

A Material is Nanocrystalline when its Crystallite Size is lower then the Interaction Length of the considered Property!

Nanocristalline/nanostructured (d < 100 nm) materials can be produced starting from:

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

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Mechanical alloying

Nanocristallins/nanostructured magnetic materials

annealing modifies the structure and the microstructure

Mechanical routes for producing nanocrystalline powders

What is mechanical alloying?

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Usually, we make alloys by melting together the components

Mechanical alloying **(MA)** involves the synthesis of materials in solid state by high-energy ball milling

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Elemental Powders Mixture

Milling in high energy ball mill

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

New phase

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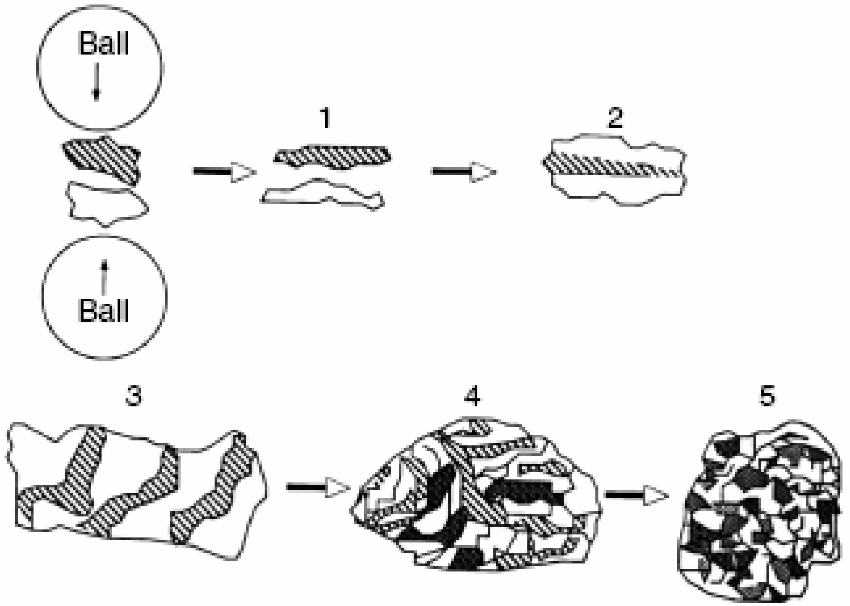

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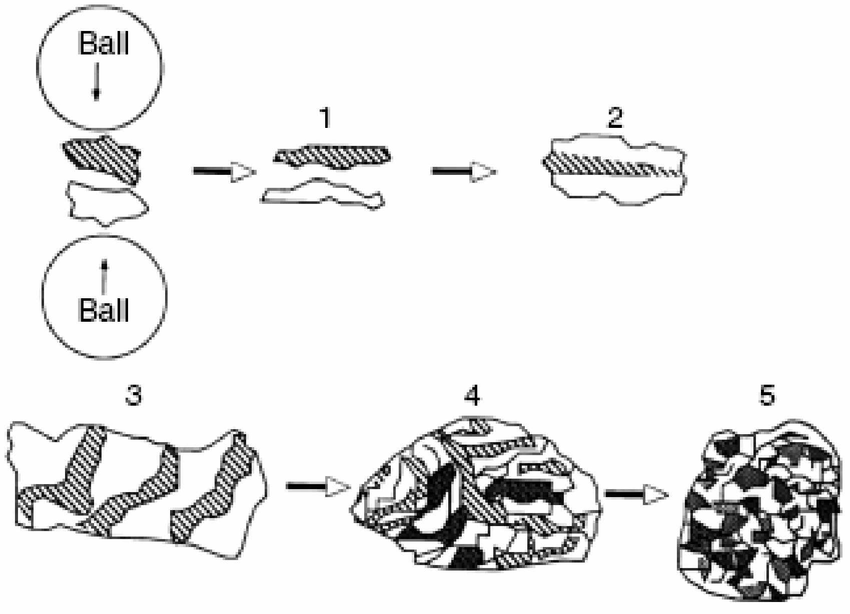
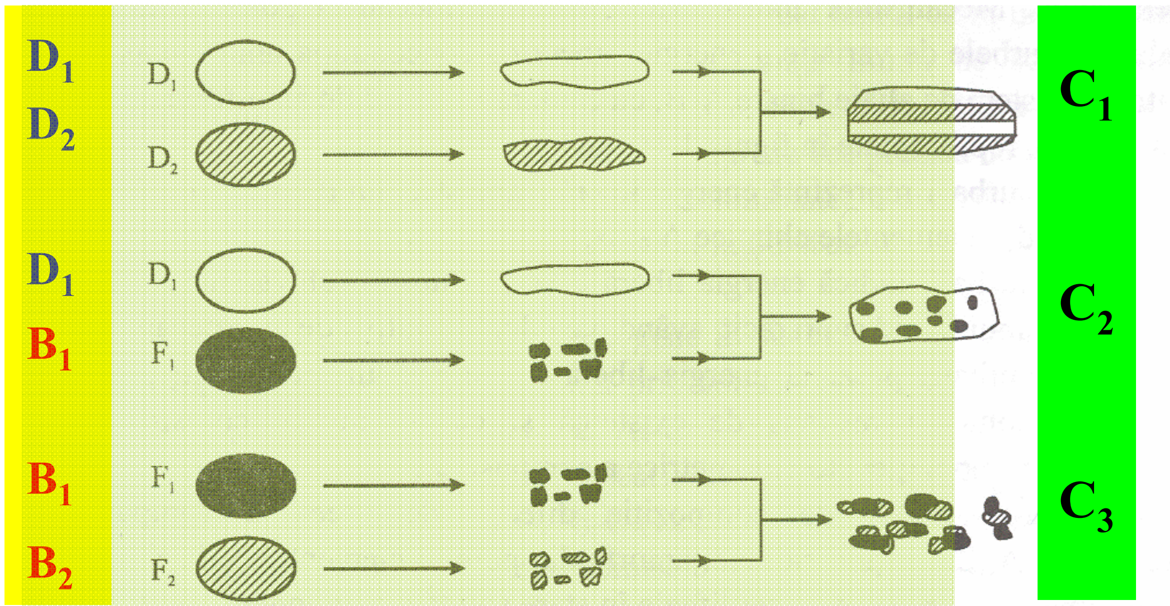
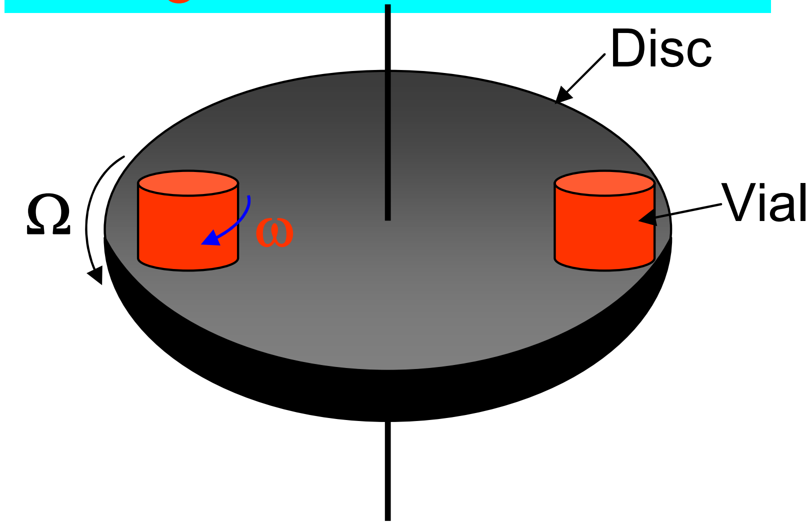




Mechanical routes for producing nanocristalline powders

Mechanical alloying **(MA)** involves the synthesis of materials by high-energy ball milling - **PROCESS**

Mechanical milling **(MM)** refers to the process of milling pure metals or compounds without solid state reaction



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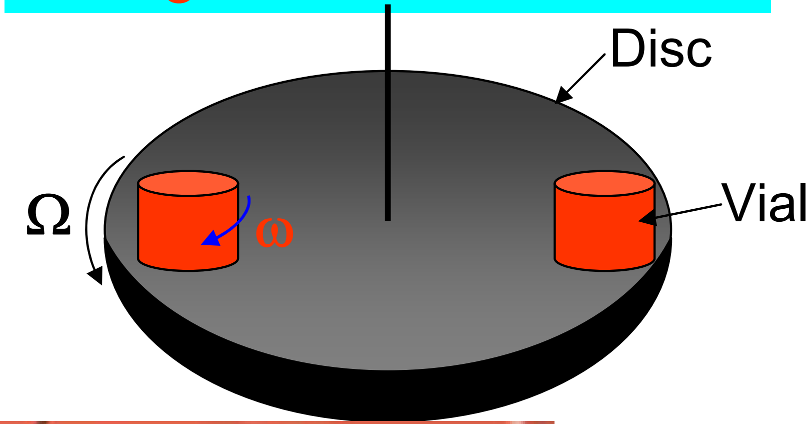

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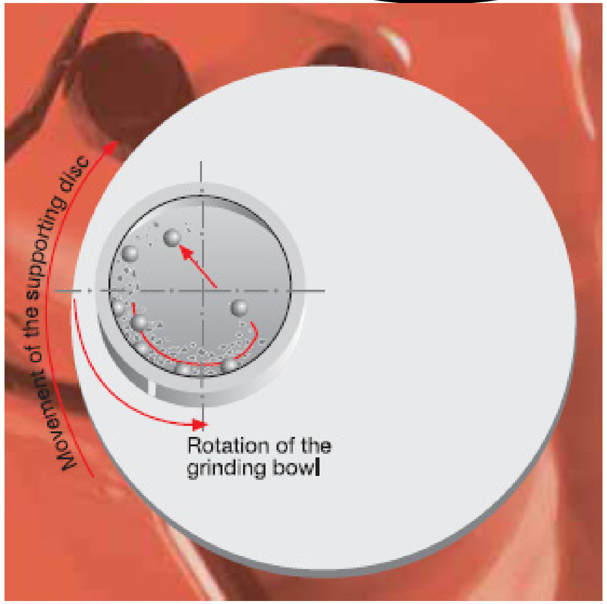

working principle

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Mechanical routes for producing nanocristalline powders

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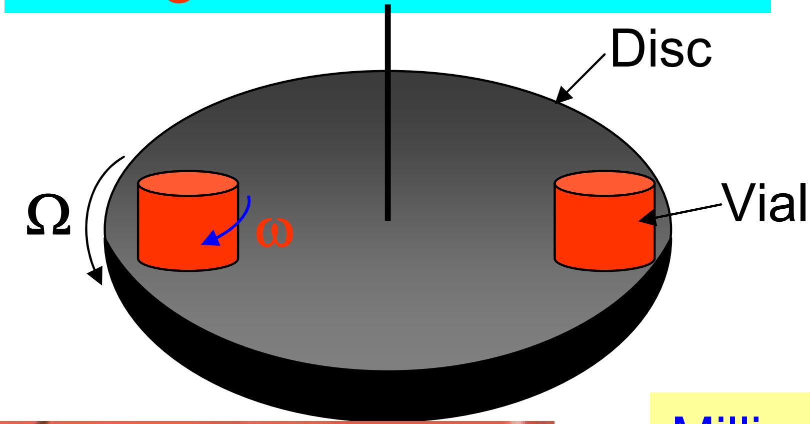

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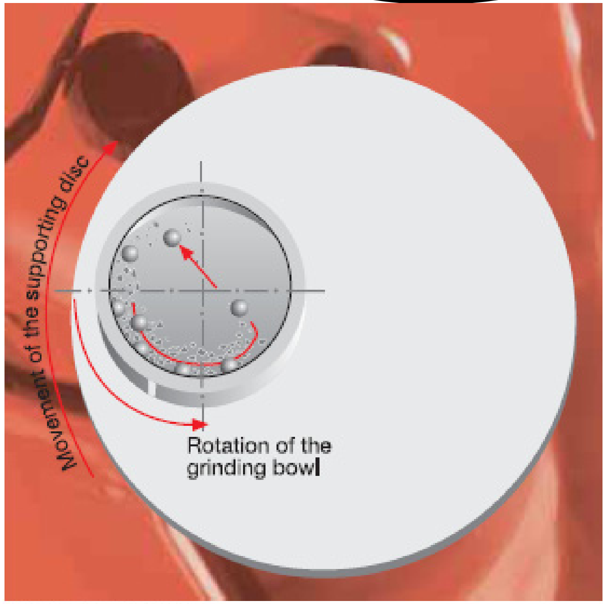
Milling:
- Dry milling
- Wet milling
- Cryomilling



working principle

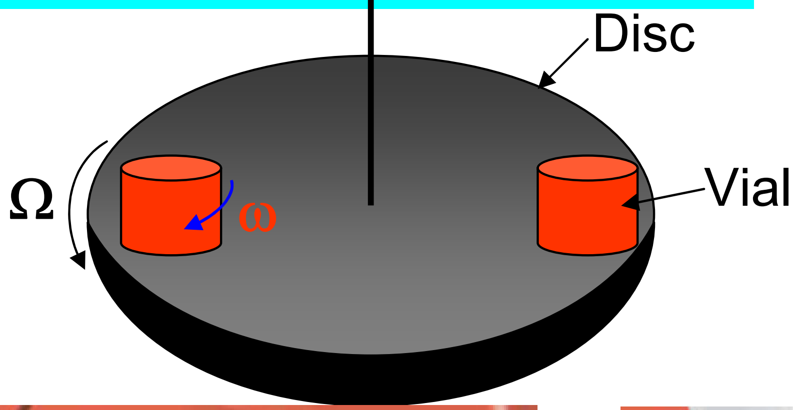
Three groups of parameters were identified, depending on:

- factors related to material or materials mixture subjected to milling.
- Factors depending upon the milling equipment, including the milling bodies
- Factors depending upon processing

Mechanical routes for producing nanocristalline powders

Mechanical alloying **(MA)** involves the synthesis of materials by high-energy ball milling - **Equipments**

Mechanical milling **(MM)** refers to the process of milling pure metals or compounds without solid state reaction



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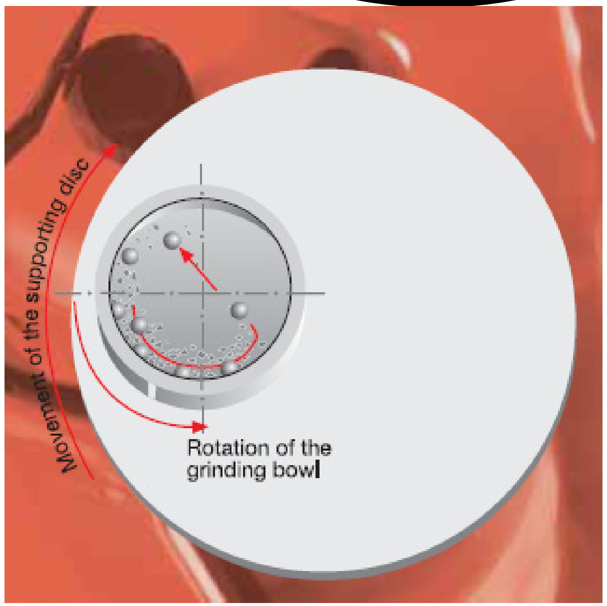
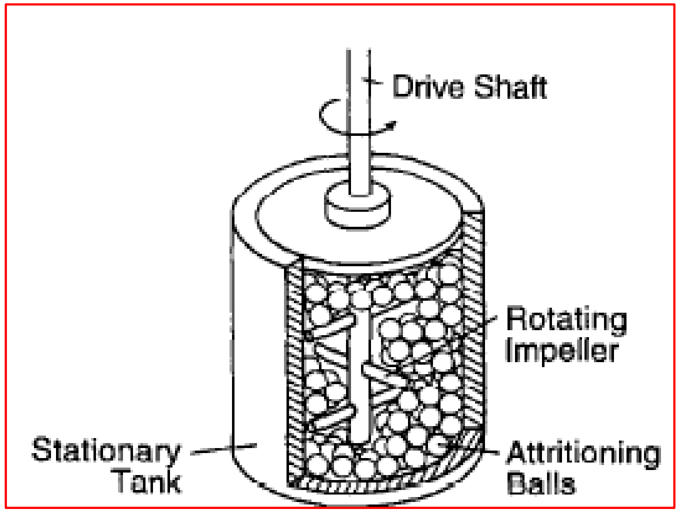


working principle


pulverisette 5 with 4 grinding bowl fasteners



Mechanical Alloying and Annealing Combining (MAAC) - What is this technique?

MA

Annealing the mixture milled

Generally, synthesis of new material by MA needs a long time

What's happening if we **STOP** the milling process before the mechanical alloying finishing and then we make an **annealing**?

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

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It is `possible to improve (finishing) the solid state reaction of compound/alloy forming!

MAAC – can reduce the synthesis time!

Reactive milling (RM)
Mechanochemistry (MC)
(dry or wet **MM)**

The MC consists of:

a. reduction of the grain size below a certain value

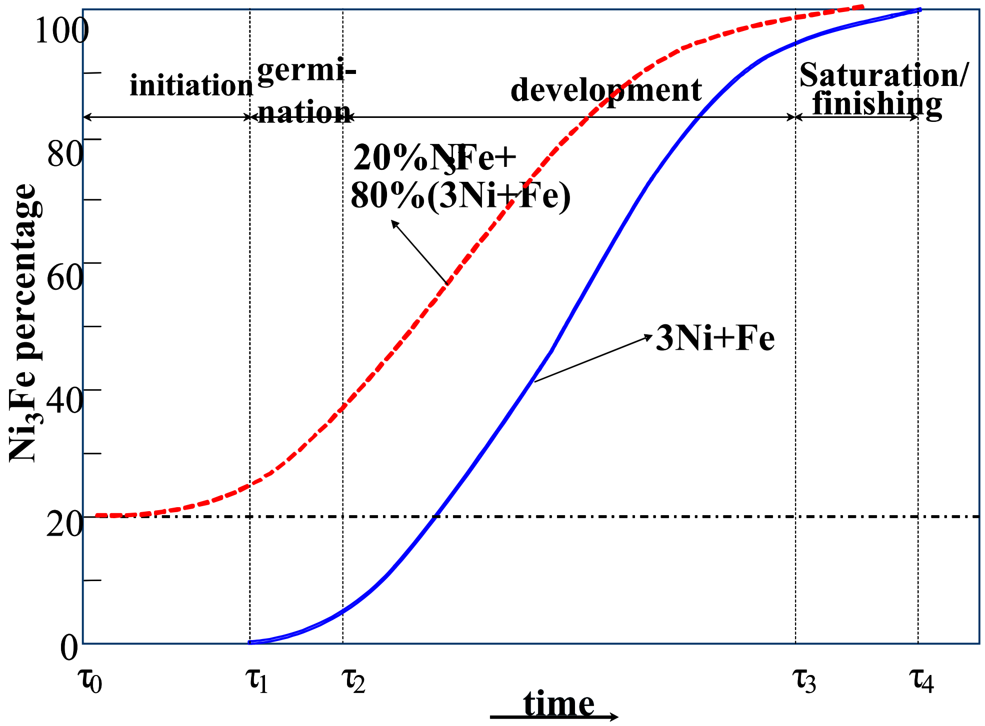
b. the subsequent chemical reaction towards the equilibrium phase composition under the milling conditions.

$$MO + R \rightarrow M + RO$$

(it is applied for oxides, chlorides, sulphurs, etc.)

Mechanical Alloying in the Presence of Nanocrystalline Germs of the same Product

$$mA + nB = A_m B_n \quad \Rightarrow \quad (1-x)\cdot(mA+nB) + x\cdot A_m B_n = A_m B_n$$



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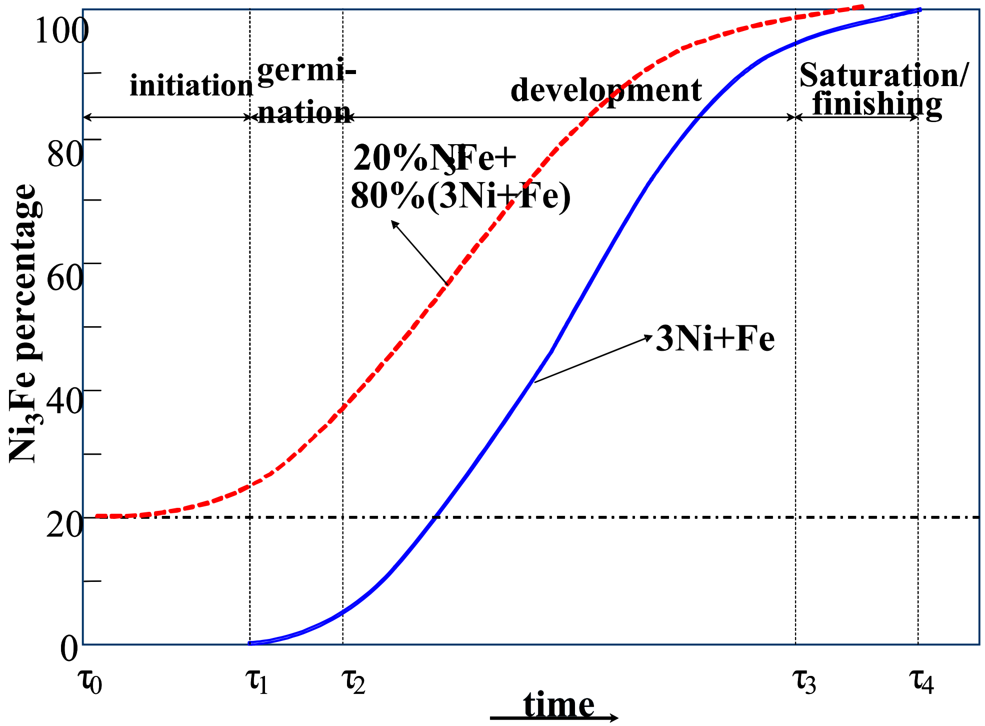
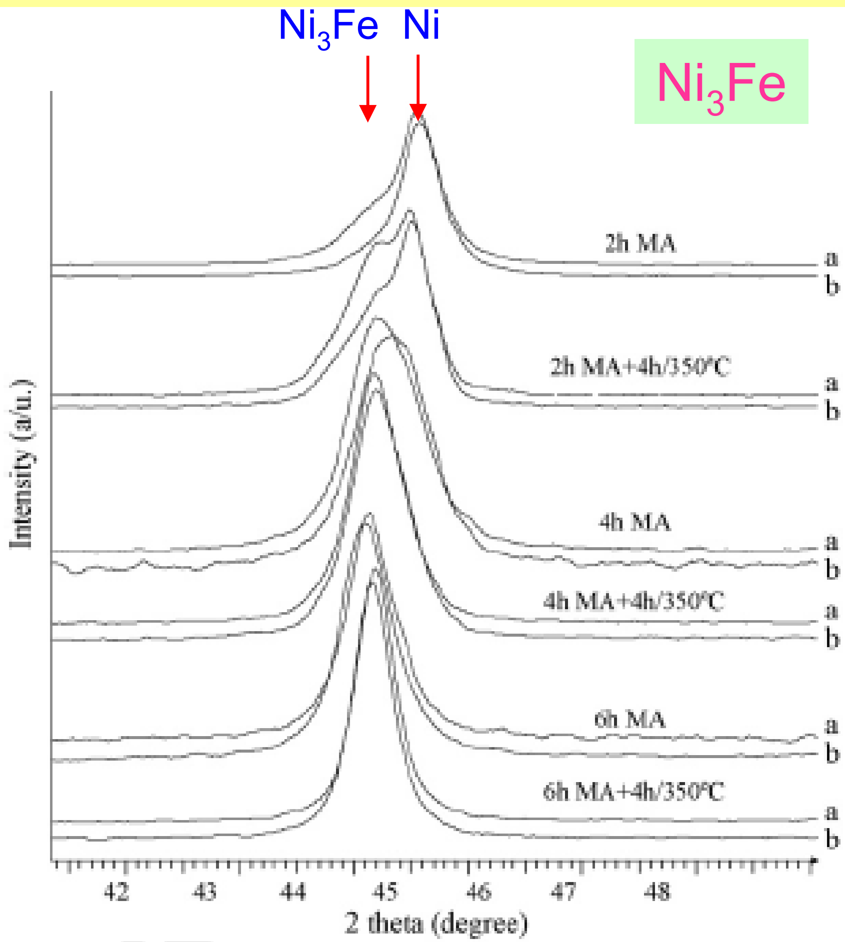




Z. Sparchez, I. Chicinas, O. Isnard, V. Pop, F. Popa, J. Alloys and Compounds, **434–435** (2007) 485–488

Mechanical routes for producing of ferrites

Polycrystalline ferrite produced by solid state reaction
(ceramic method)

Mechanical milling
(dry or wet milling)

$MeFe_2O_4$
Me = Mg, Cu, Ni,

Stoichiometric mixture of oxides or of oxides and hidroxicarbonate

Mechanochemistry
(dry or wet milling)

$MeFe_2O_4$, Me = Mn, Cu, Zn, Ni

≈80-95 %
spinel phase

Annealing produces only spinel phase

$ZnFe_2O_4$

Low temperature chemical co-precipitation
(nanosized ferrite)

Mechanical milling
(dry or wet milling)

$ZnFe_2O_4$, $CuFe_2O_4$,

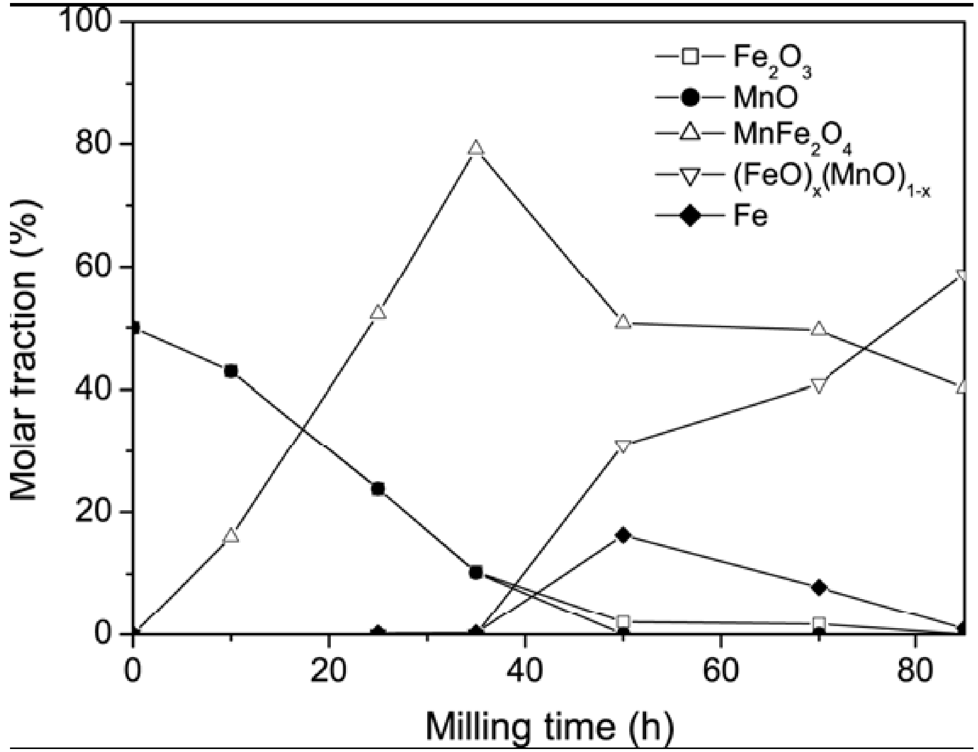
Soft magnetic nanocrystalline (nanosized) ferrites

Structural properties, phase composition

Partial reversibility during milling of the reaction:

$$\alpha\text{-}Fe_2O_3 + MeO \leftrightarrow MeFe_2O_4$$

The particles contain several related Fe–Me–O phases



Milling in closed vial:
$\alpha\text{-}Fe_2O_3$ is reduced at Fe_3O_4

Milling in open vial:
neither reduction of Fe^{3+} were detected

Particle size is generally reduced under 10 nm

G.F. Goya, H.R. Rechenberg, J. Phys: Condens. Mater., **10** (1998) 11829-11840
G.F. Goya, H.R. Rechenberg, J.Z. Jiang, J. Appl. Phys. **84** (1998) 1101-1108
F .Padella et al. Mater. Chem. Phys. **90** (2005) 172-177

Magnetic behaviour of mechanosyntesized ferrites

The magnetic properties are associated with

- the canted spin configuration in small particles
- the non-equilibrium cation redistribution resulting in a decrease of the number of magnetic $Fe^{3+}(A)$-O^{2-}-$Fe^{3+}(B)$ linkages

Magnetisation does not saturated even in an applied field of 9 T
Ms decrease with milling time as a result of spin canting effect

The hysteresis loop is not symmetrical about the origin and is shifted to the left → ΔH_C which increases with increasing the milling time

Coexistence of both ferrimagnetic and superparamagnetic phase

Mechanical routes used for producing SMA

MA

MC*
- MM of oxides blend
- reduction of oxides
- alloying by heat treatment

MAAC

Two-step MA
- obtaining nanocrystalline alloy by MA
- obtaining nanocrystalline alloy by MM

MAAC with inoculated germs

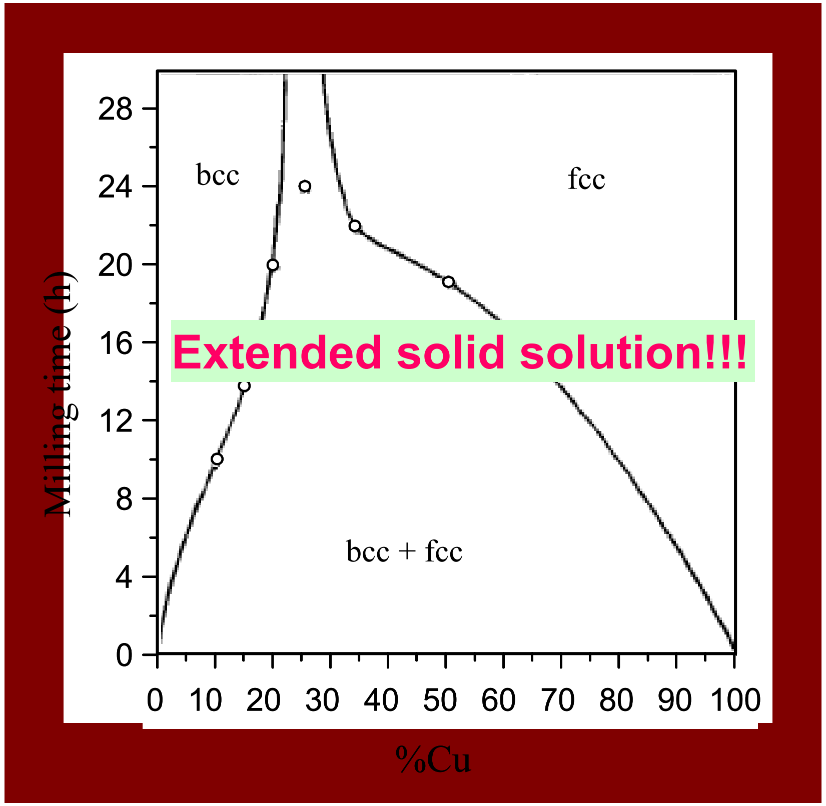
Raw materials used – generally elemental powders
Milling equipment used - generally planetary ball mill
Ball/powder mass ratio : very different (from 5:1 to 30:1)

Soft Magnetic Nanocrystalline Powders

*X.Y. Qin, S.H. Cheong, J.S. Lee, Mater. Sci. Eng., **A 363** (2003) 62

Fe-Cu powders obtained by MA

Milling map of mechanically alloyed Fe-Cu system



B. Majumdar et al., J. Alloys Comp. **248**, 192 (1997)

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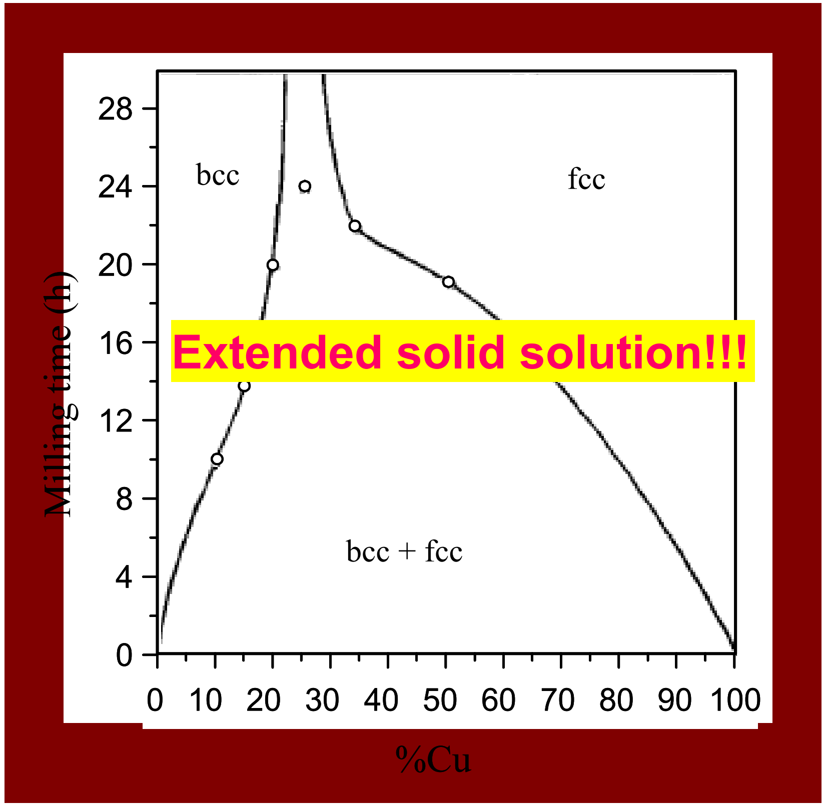
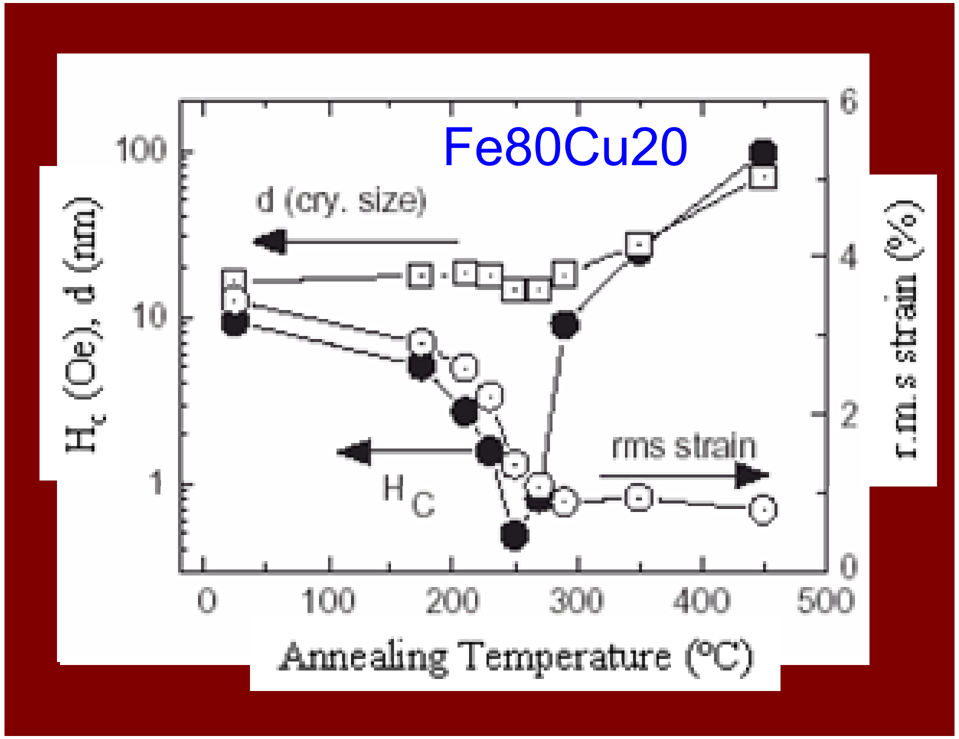


B. Majumdar et al., J. Alloys Comp. **248**, 192 (1997)

Interesting magnetic properties



R.B. Schwarz, T.D. Shen, U. Harms, T. Lollo, J. Magn. Magn. Mater. **283**, 223 (2004).

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

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

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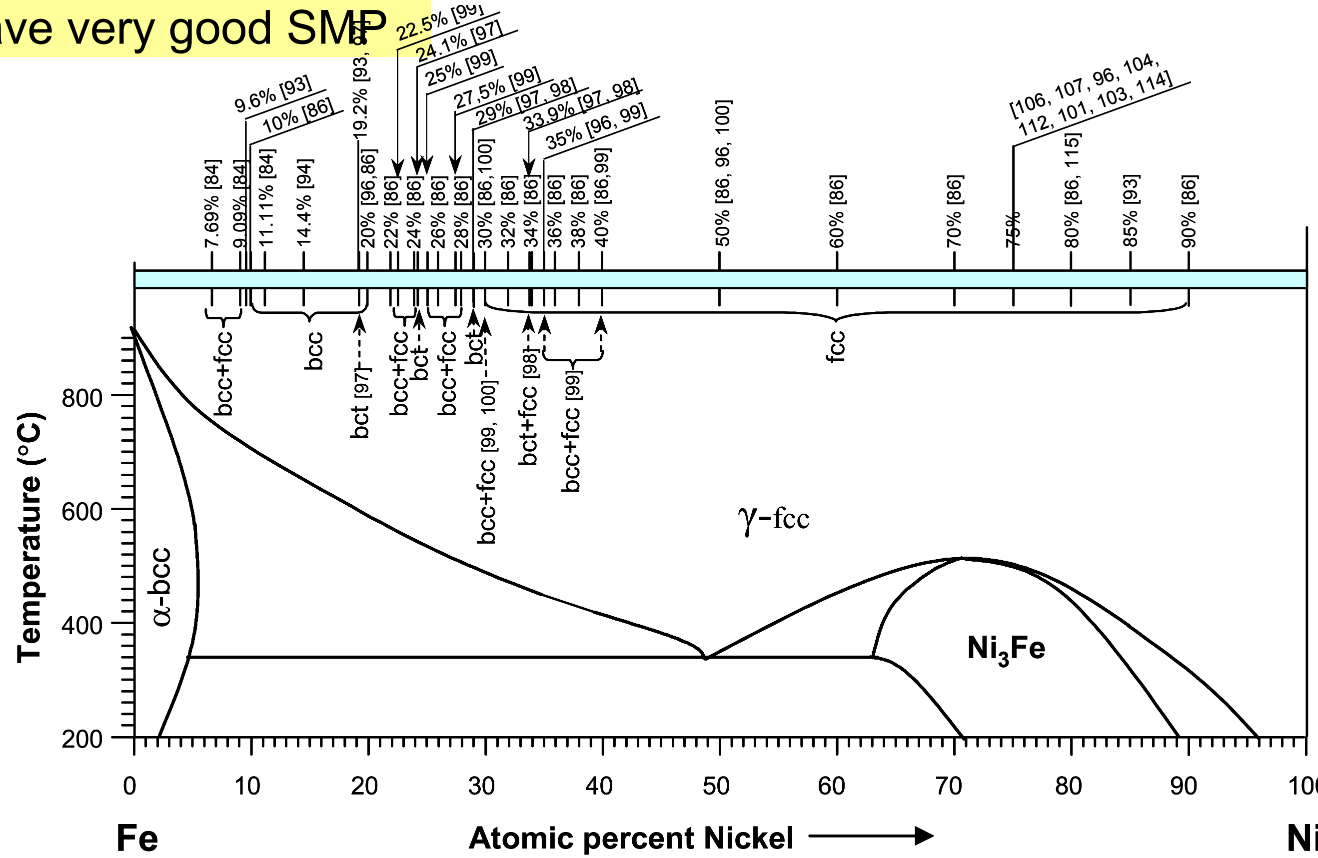


V. Pop, I. Chicinaş, J. Optoelectron. Adv. Mater. **9** (2007), 1478-1491

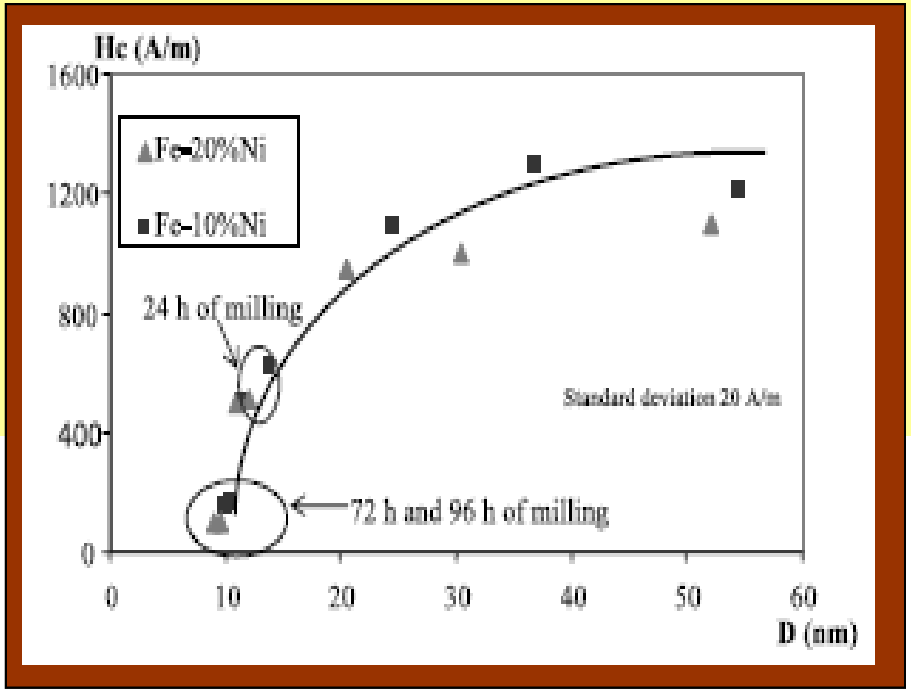
Properties depending of milling conditions

It has been proved that the milling performed in the friction mode (FMP) leads to the formation of alloys exhibiting a soft magnetic behaviour. However, magnetisation is not affected by the mode used

R. Hamzaoui, O. Elkedim, E. Gaffet, J. Mater. Sci., **39** (2004) 5139

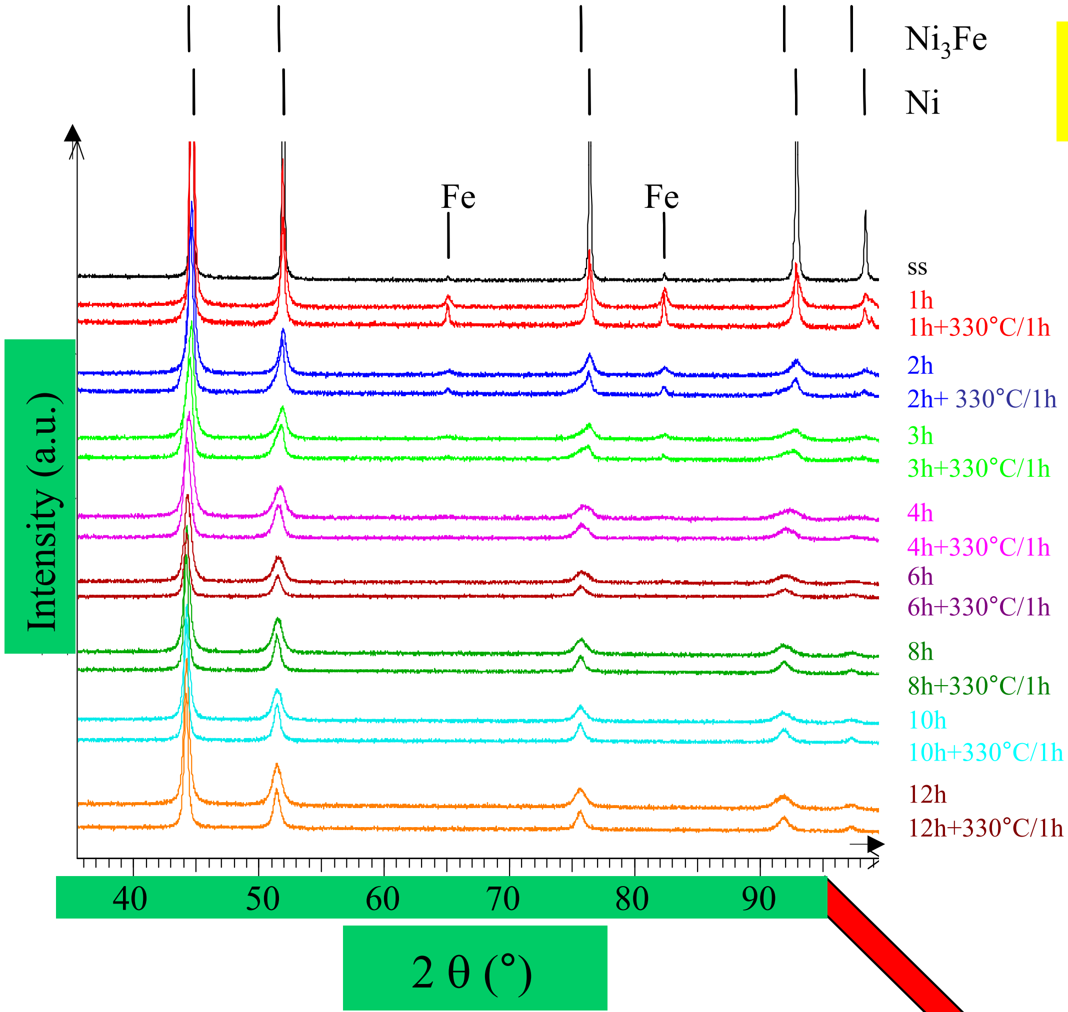
In high-energy ball milling process the fcc solid solution γ(Fe,Ni) in alloys Fe65Ni35 was formed after 36 hours, while in the low-energy milling process the Fe lines disappeared after 400 hours of milling.

E. Jartych, J.K. Żurawicz, D. Oleszak, M. Pękała, J. Magn. Magn. Mater. **208** (2000) 221



A strong decrease of the coercive field versus crystallite size appears especially for crystallite size smaller than 20 nm

R. Hamzaoui, O. Elkedim, N. Fenineche, E. Gaffet, J. Craven, Mater. Sci. Eng. A 360 (2003) 299-305



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

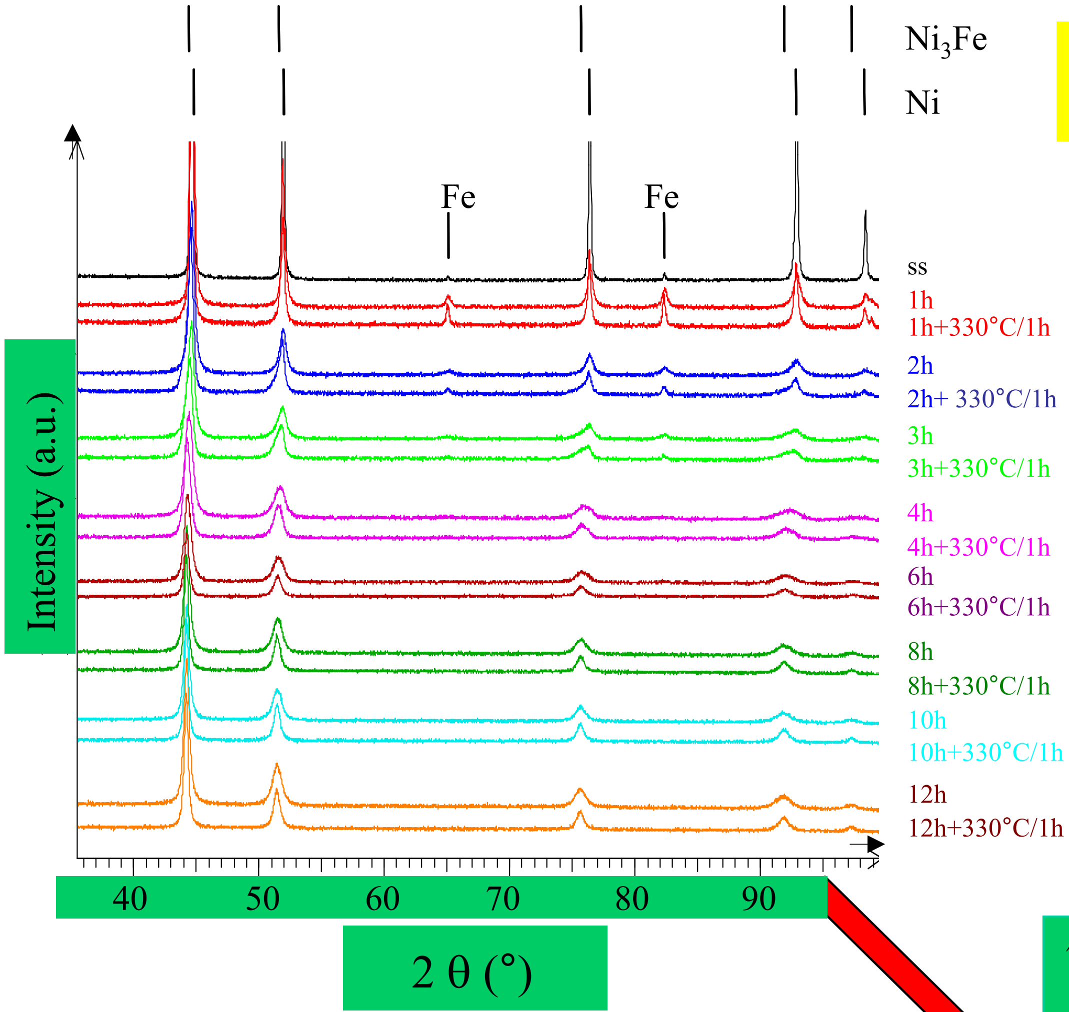
peaks shift to **LOWER** 2θ angles

peaks shift to **HIGHER** 2θ angles

relaxion of the first order internal stresses

the **second order** internal stresses
Crystallite size reduction

broadening of the diffraction peaks



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

peaks shift to **LOWER** 2θ angles

peaks shift to **HIGHER** 2θ angles

relaxion of the first order internal stresses

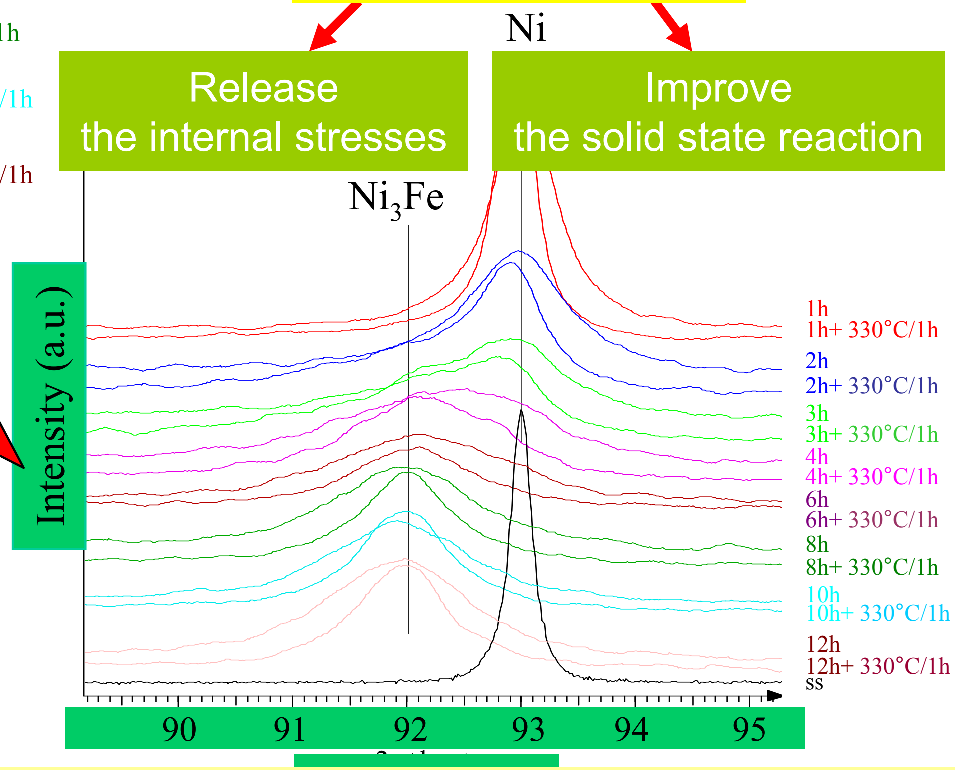
Annealing effect

Release the internal stresses

Improve the solid state reaction

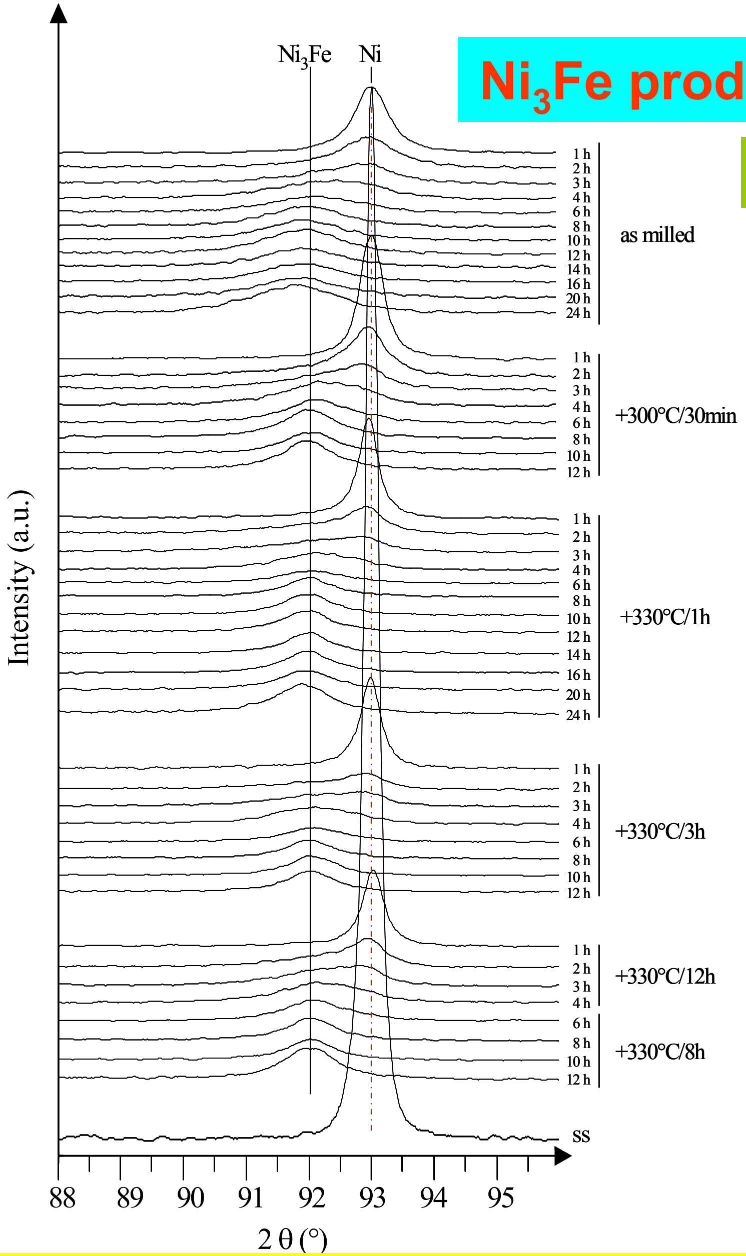
the **second order** internal stresses
Crystallite size reduction

broadening of the diffraction peaks

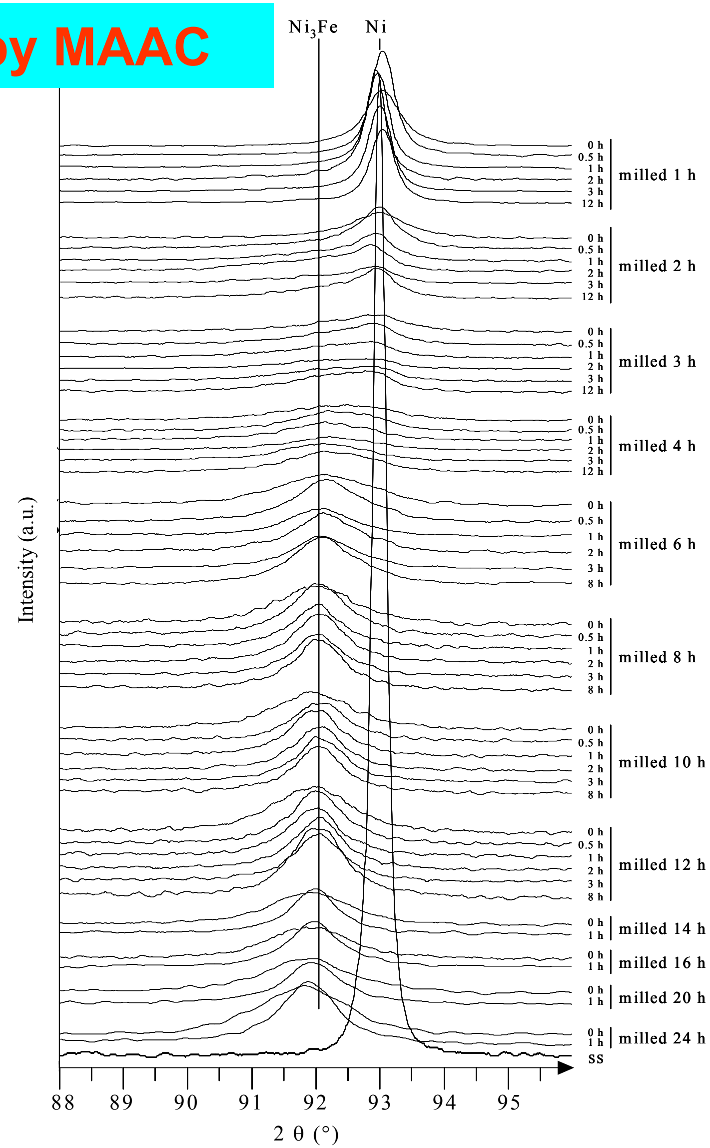


Ni_3Fe produced by MAAC

(311)

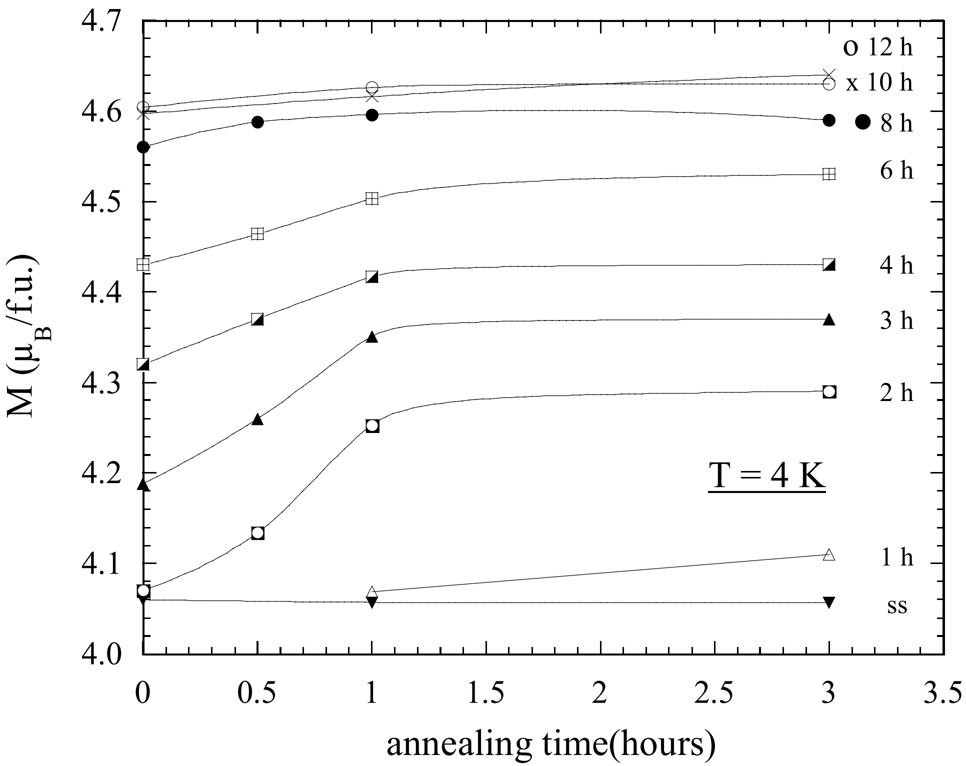


One annealing time - Different milling time



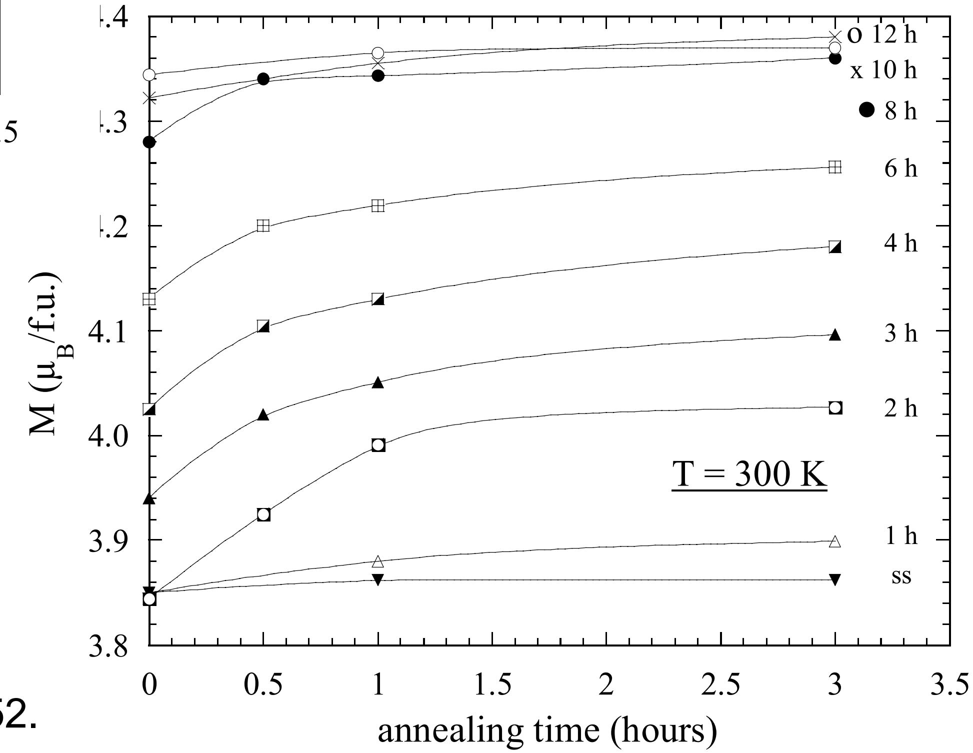
One milling time - Different annealing time

Mean grain size : 15 ± 2 nm , after 32 h milling

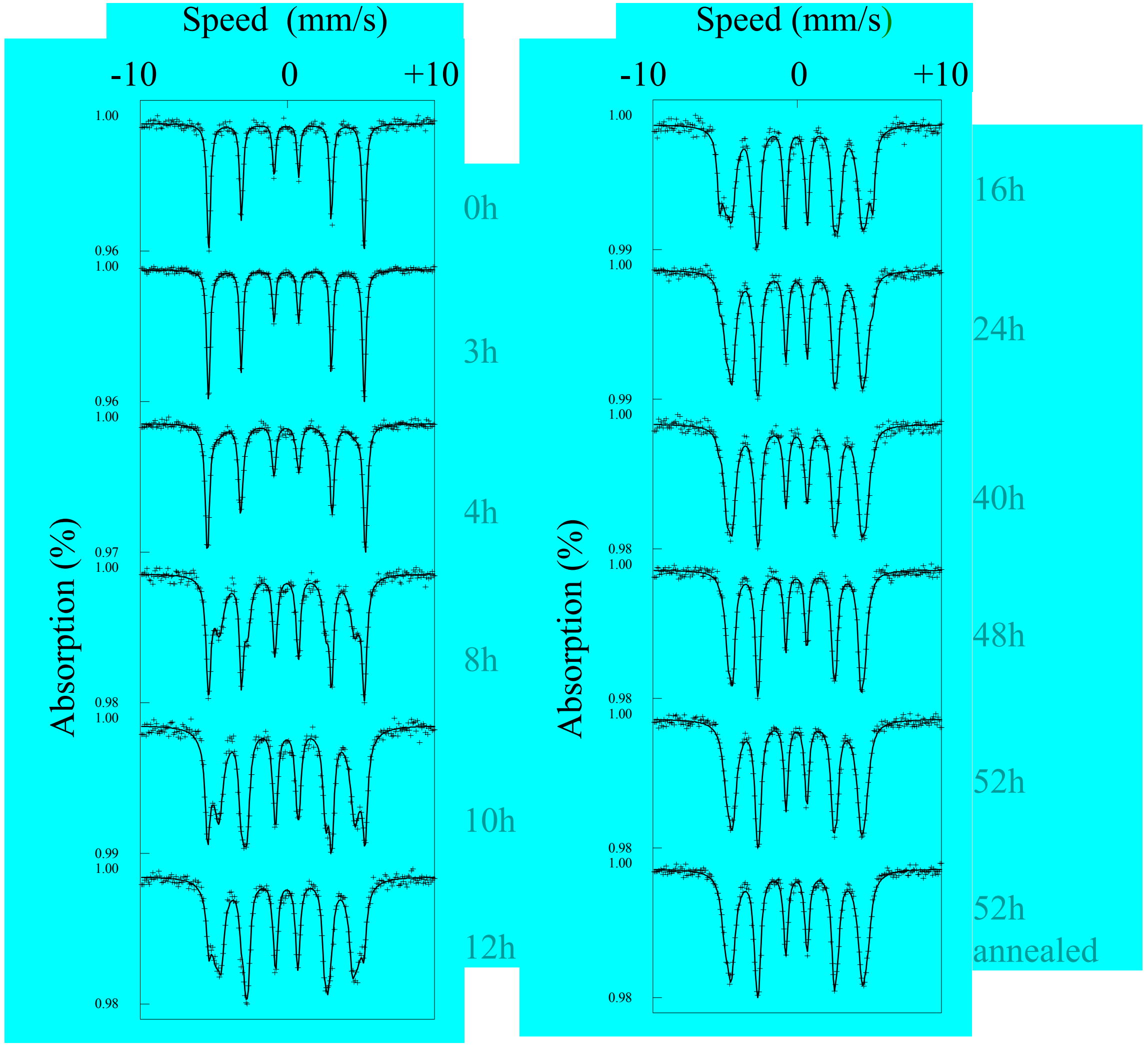


Ni_3Fe produced by MAAC

Influence of the milling and annealing conditions on the M_s



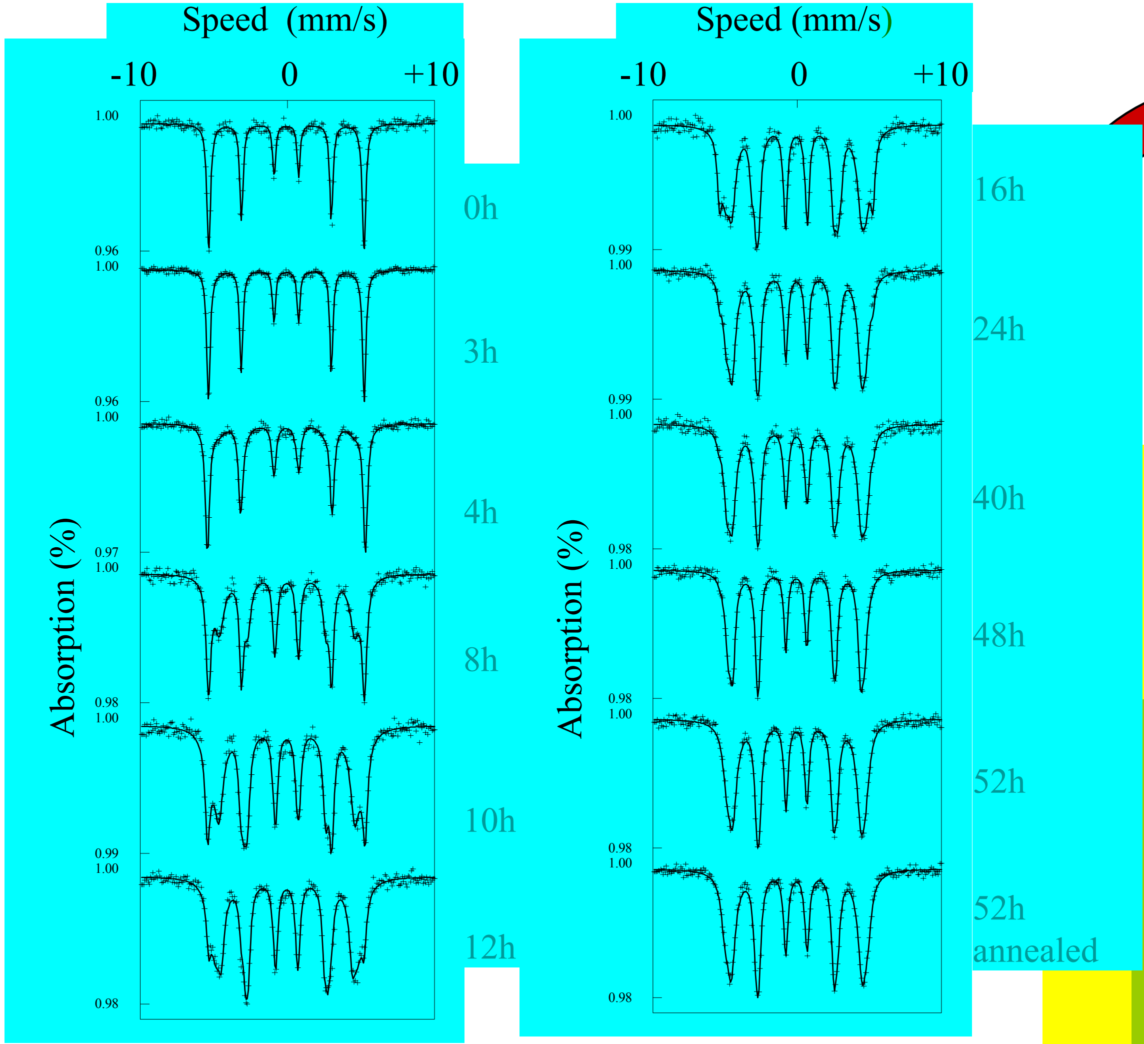
V. Pop, O. Isnard and I. Chicinas,
J. Alloys and Comp., **361** (2003), p.144-152.

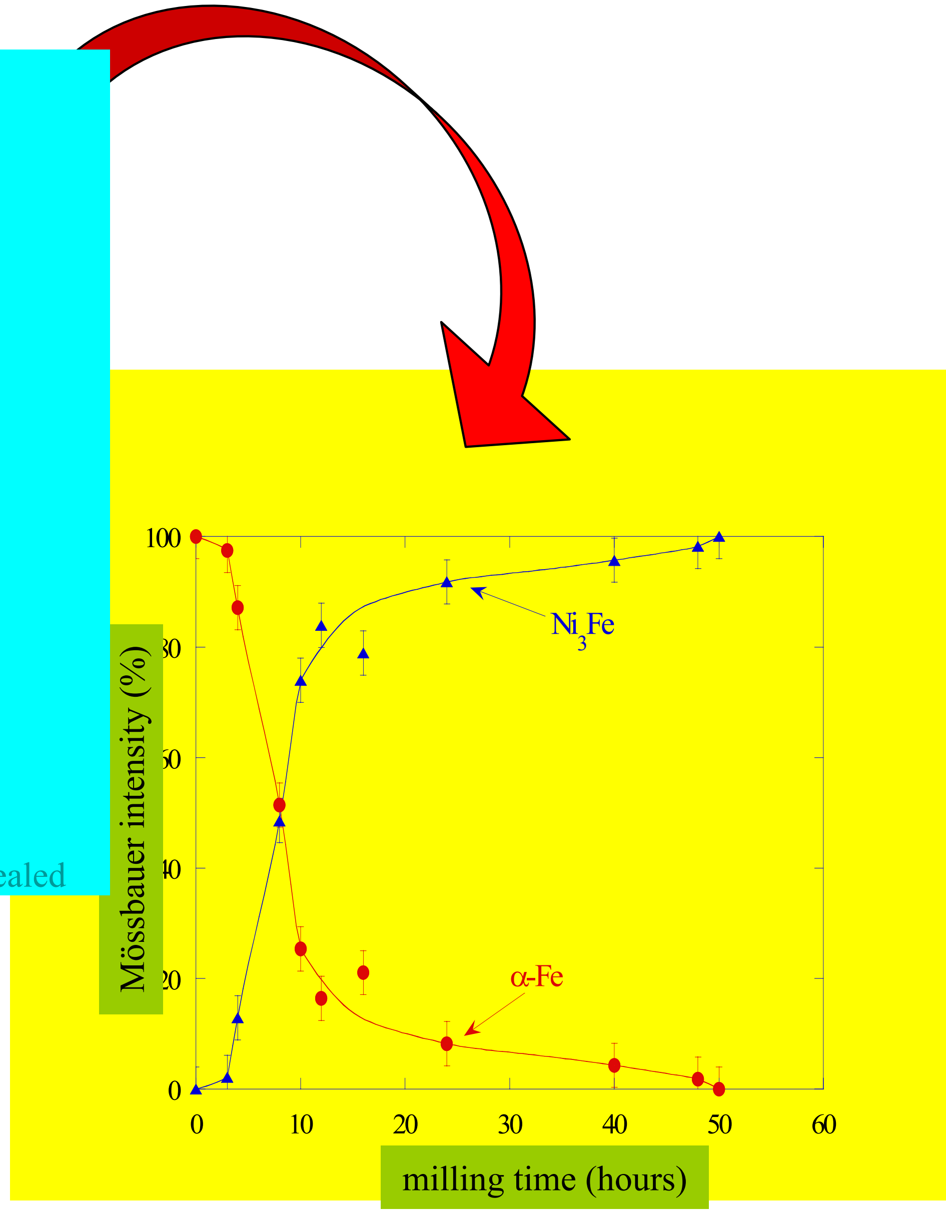


Mössbauer spectrometry

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





Mössbauer spectrometry

Ni_3Fe powders

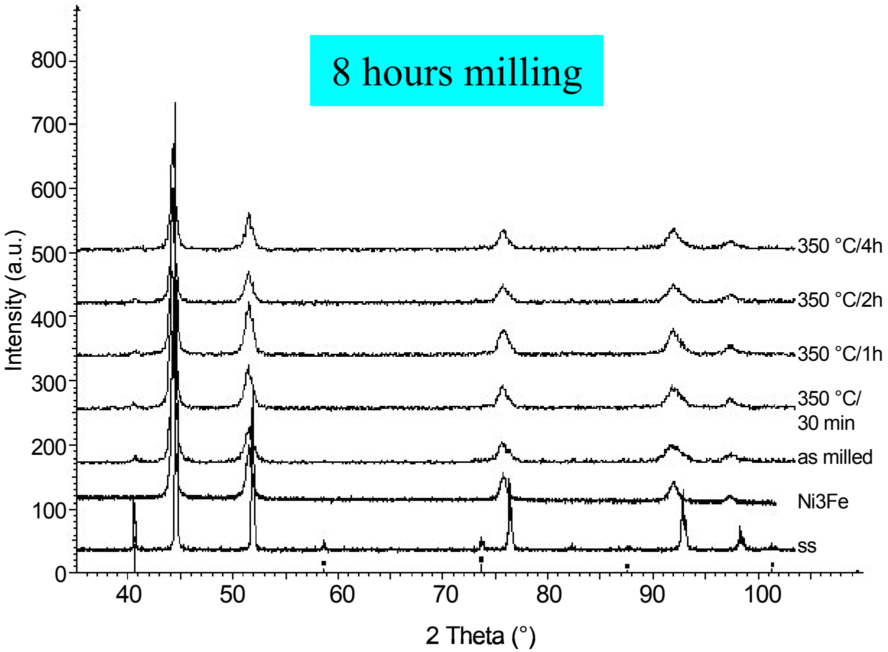
I. Chicinas, V. Pop, O. Isnard, J.M. Le Breton and J. Juraszek, J. Alloys and Compounds 352 (2003), p. 34-40

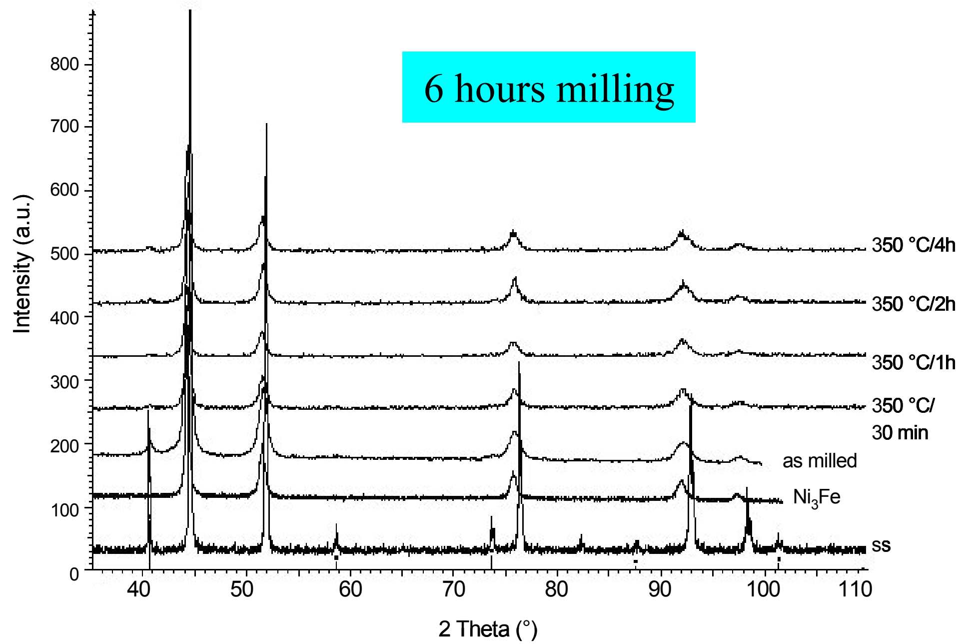
Nanocrystalline soft magnetic powders from Fe-Ni-X-(Y) systems

FeNi3)xAg1-x, Ni50Al50-xFex , Fe49Ni46Mo5, Fe42Ni40B18 , Ni-15%Fe-5%Mo and Ni-16%Fe-5%Mo (wt%), Ni-14%Fe-5%Cu-4%Mo and others

Supermalloy synthesis by MAAC:

- 8 hours milling
- different annealing conditions.





$$d = \frac{k \cdot \lambda}{\beta_{\frac{1}{2}} \cdot \cos\theta}$$

$\beta_{\frac{1}{2}}$ - FWHM

d = { **11 nm** - 16 h milling and annealing at 350 °C for 2 hours in order to remove second order internal stresses

I. Chicinas, O. Isnard, V. Pop, J. Mater. Sci. **39** (2004), p. 5305-5308
O. Isnard, V. Pop, I. Chicinas, J. Magn. Magn. Mater. **290-291** (2005), p. 1535-1538.

Alliage 77Ni14Fe5Cu4Mo % massique

10h : seule la T_c de l'alliage est observée
le traitement thermique homogénéise

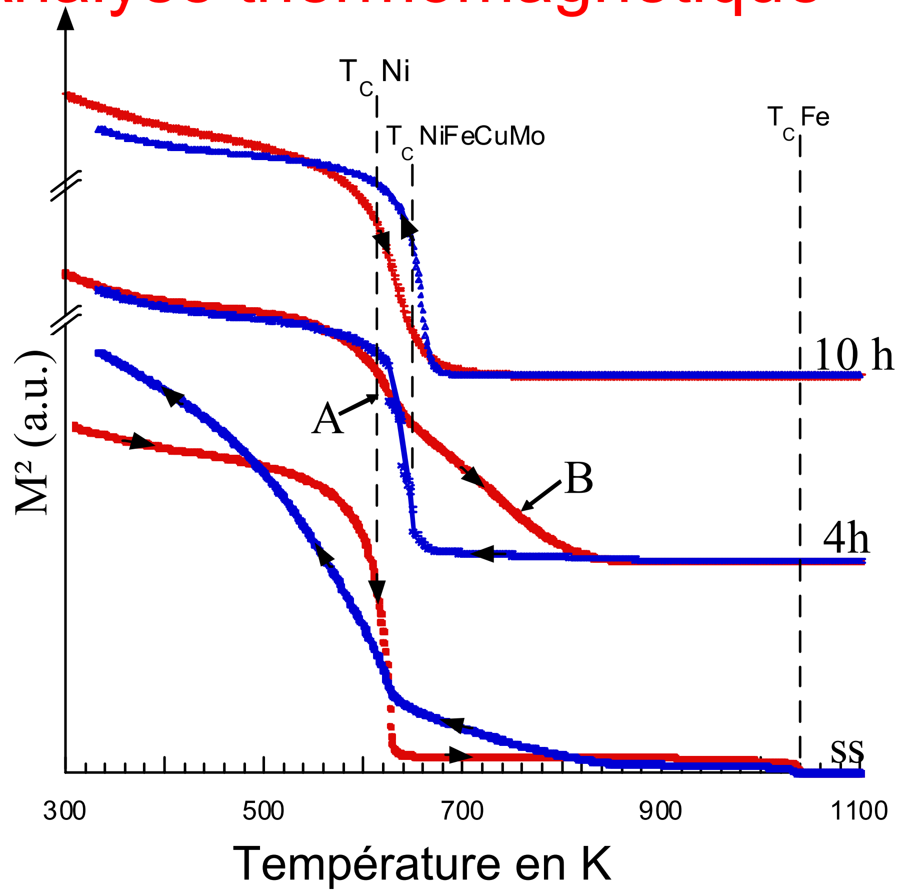
4h : -Chauffage changement de pente au point A correspond à T_c de NiFeCuMo obtenu par broyage

-Formation progressive de l'alliage par chauffage (région B)
Large domaine de composition

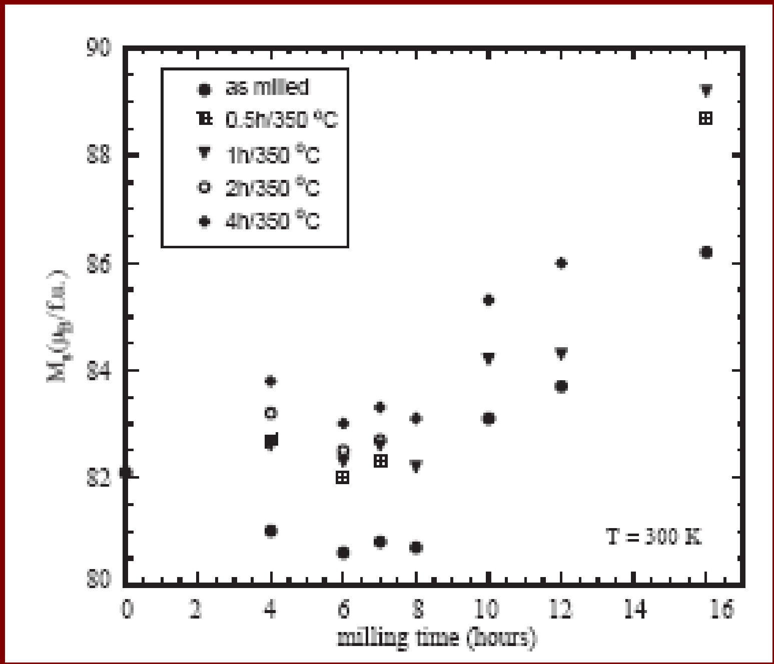
-Refroidisement une seule T_c détectée alliage formé dans le volume

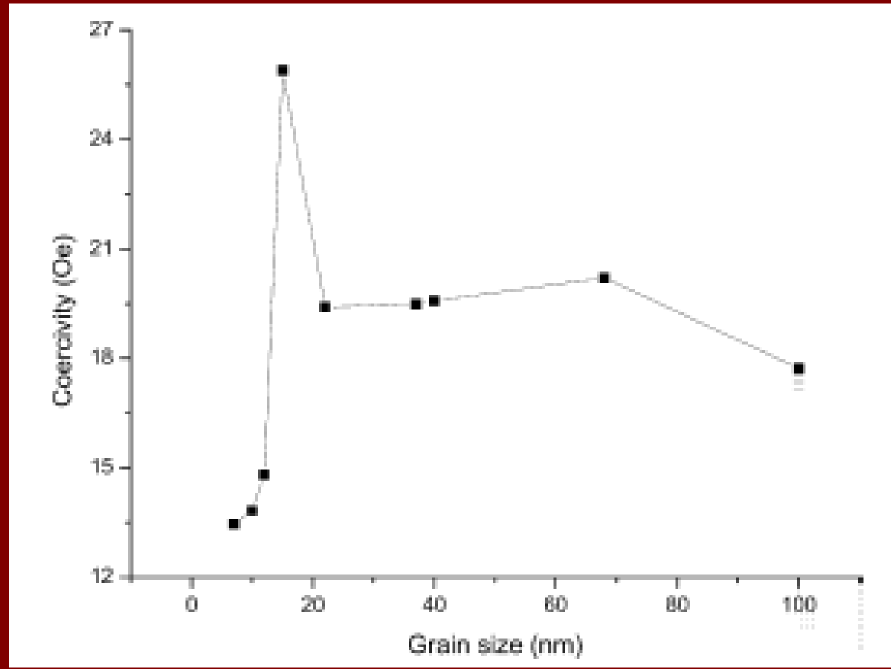
SS : Mélange de départ T_c de Ni et Fe

Analyse thermomagnétique



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





the mechanical alloying process occurs in two steps

an intermediate amorphous or poorly crystallined phase, (Ni,Fe)–Mo type.

The high coercivity before 10 h of milling is attributed to strong pinning of domain walls of the interaction domains at the grain boundaries.

O. Isnard, V. Pop, I. Chicinaş,
J. Magn. Magn. Mater. **290-291** (2005) 1535

Y. Shen, H.H. Hng, J.T. Oh,
J. Alloys Comp. **379** (2003) 266-271.

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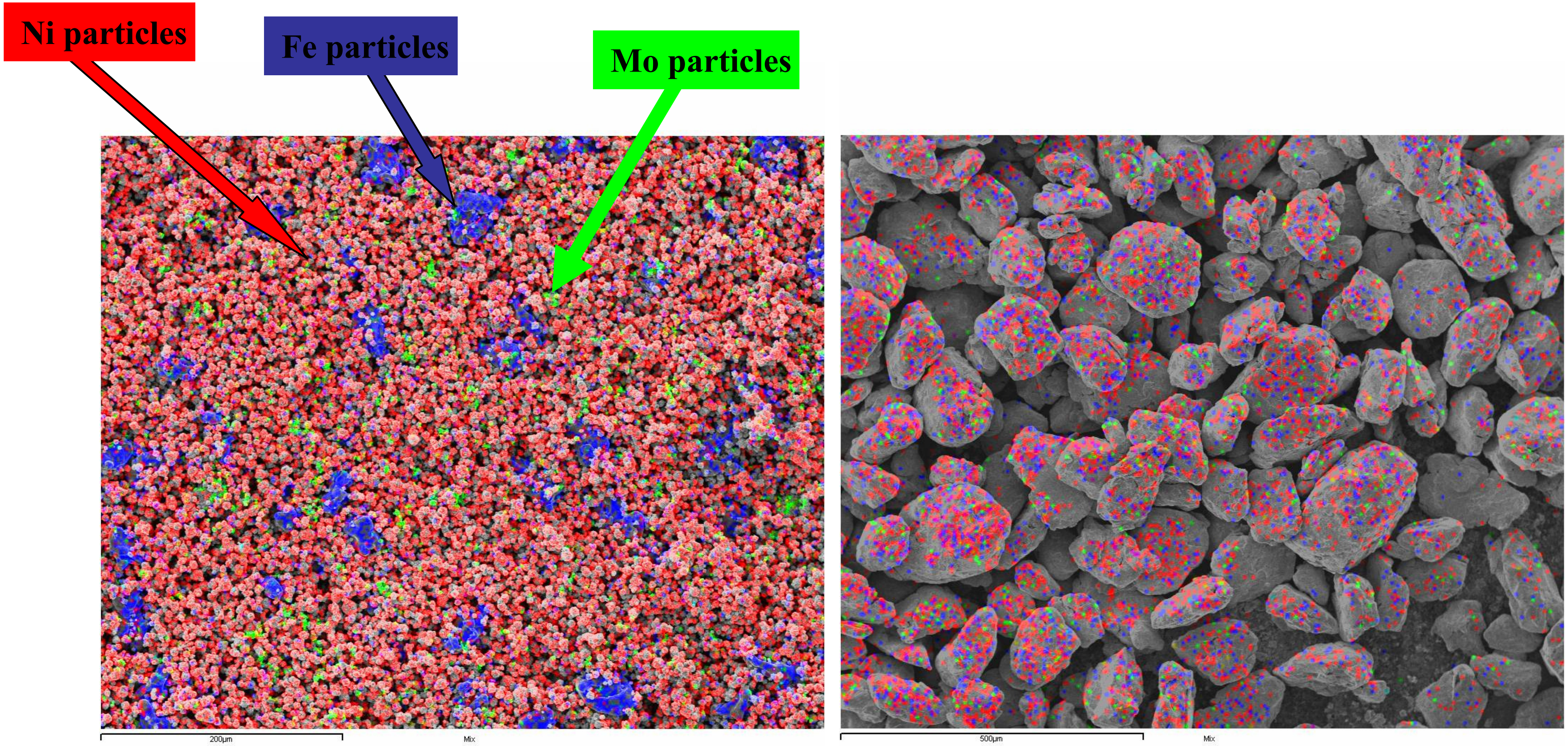
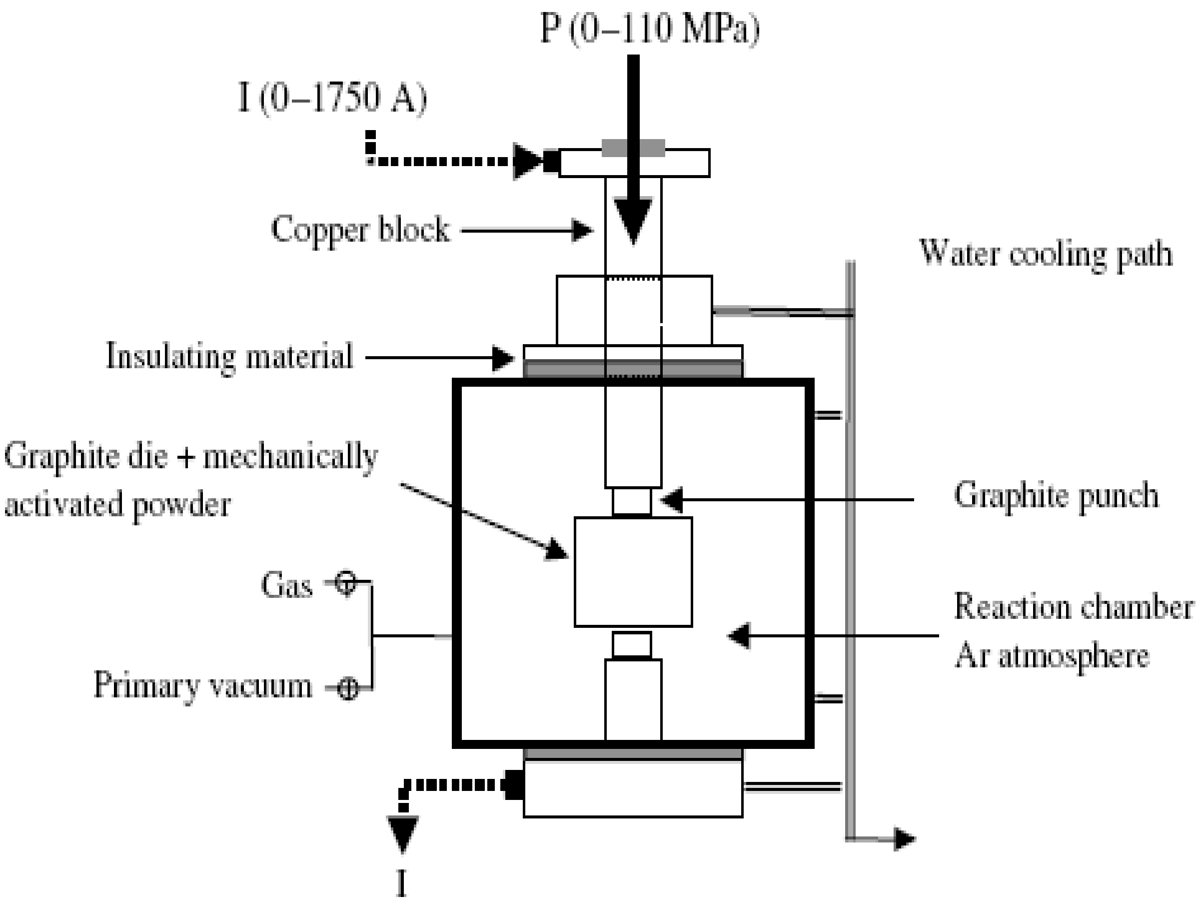


The Ni, Fe and Mo maps on starting sample (0 hours milling) and on the 12 hours milled sample. It can observe the chemical homogeneity of the Supermalloy powders obtained by mechanical alloying and the particles morphology, too.

Methods to produce from the nanocrystalline powders a a nanocrystalline compact



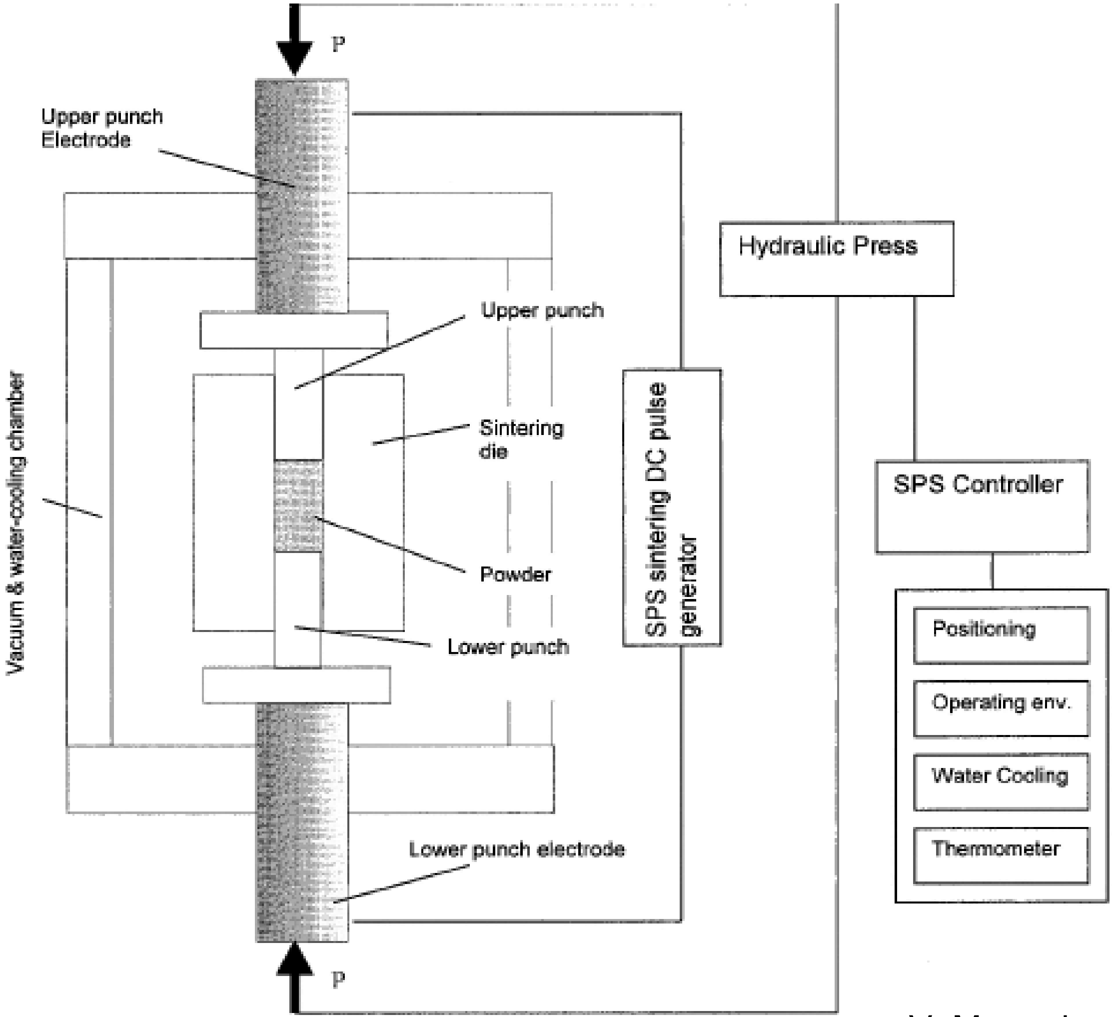
FAPAS

Field activated pressure assisted sintering. Compared to a classical sintering process under pressure, a current is applied in order to assist the sintering.

A current exhibiting a high intensity (up to 8,000 A) under low voltage (10 V) is applied.

E. Gaffet, G. Le Caër, Mechanical Processing for Nanomaterials, in Encyclopaedia of Nanoscience and Nanotechnology, vol.X, Ed. by H.S. Nalwa, American Sci. Publishers (2004).

Methods to produce from the nanocrystalline powders a a nanocrystalline compact

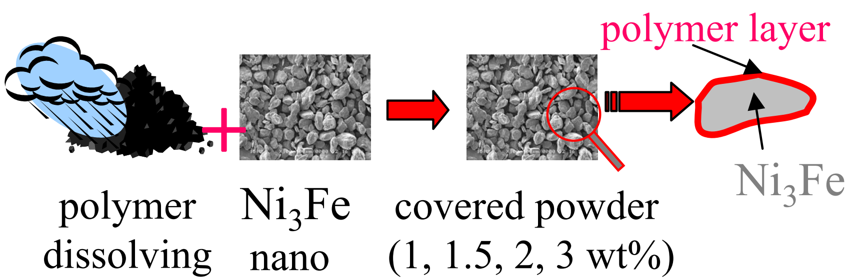


Spark plasma sintering
A process leading to bulk materials by a sintering step using pulse electric discharge.
Due to the high intensity of the current, plasma may occur between the various powder grains.

V. Mamedov, Powder Metallurgy 2002 Vol. 45 No. 4, 322-327

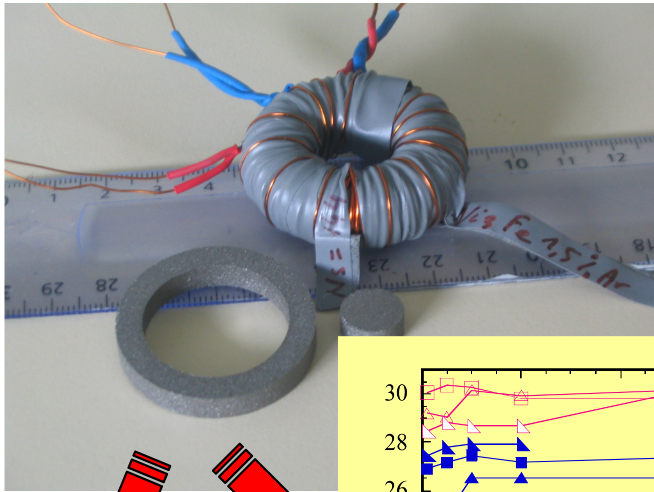
Soft magnetic nanocrystalline composites

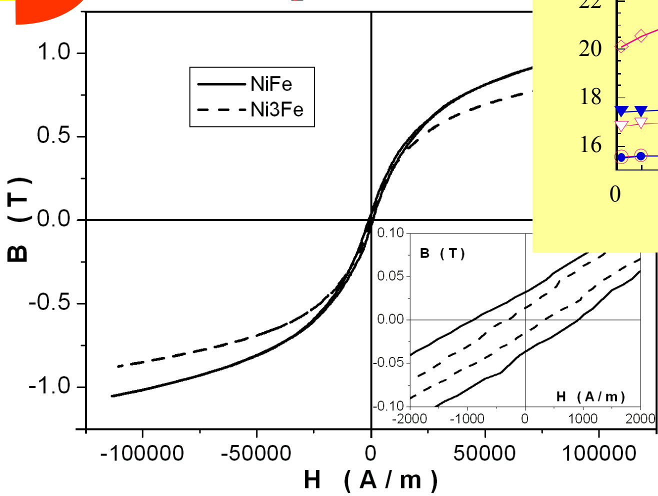
Composites Production

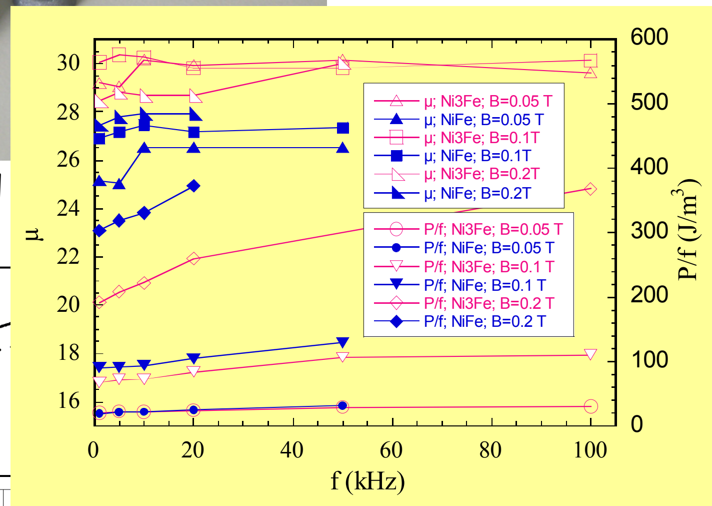


Die pressed (600 - 800 MPa)

Polymerisation (60 min., 180 °C)







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

Conclussions

The possibility of producing chemical transformations through mechanical energy has been extensively demonstrated in metallic as well as in oxide systems

The nanocrystalline/nanosized powders obtained by different mechanical routes exhibit very interesting properties, some from them different from those of bulk materials

Thank you for your attention!