Properties of soft magnetic composite compacts produced by spark plasma sintering from pseudo core-shell powders like Me@MeFe_2O_4 type

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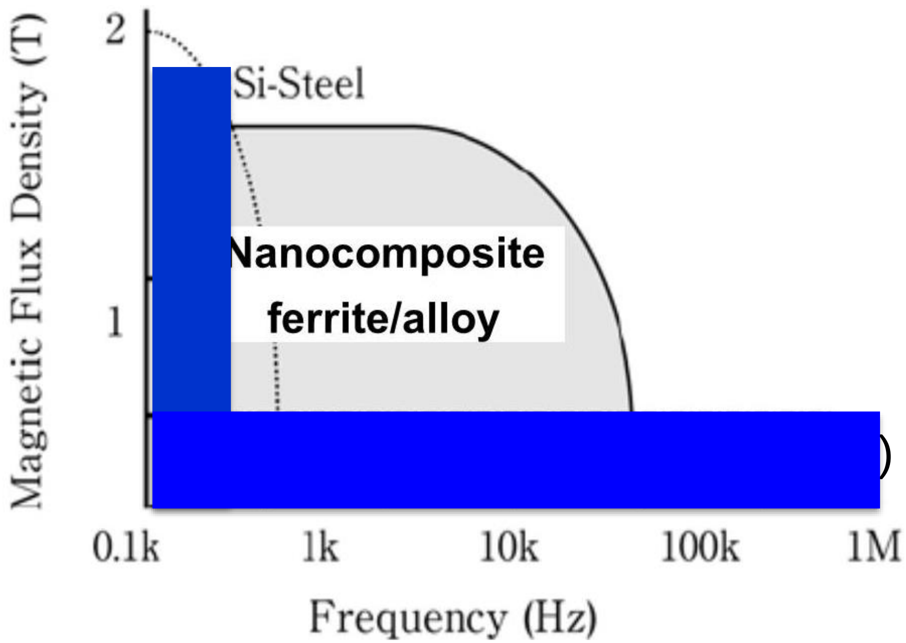
MagMatNano magnetic materials and nanomaterials

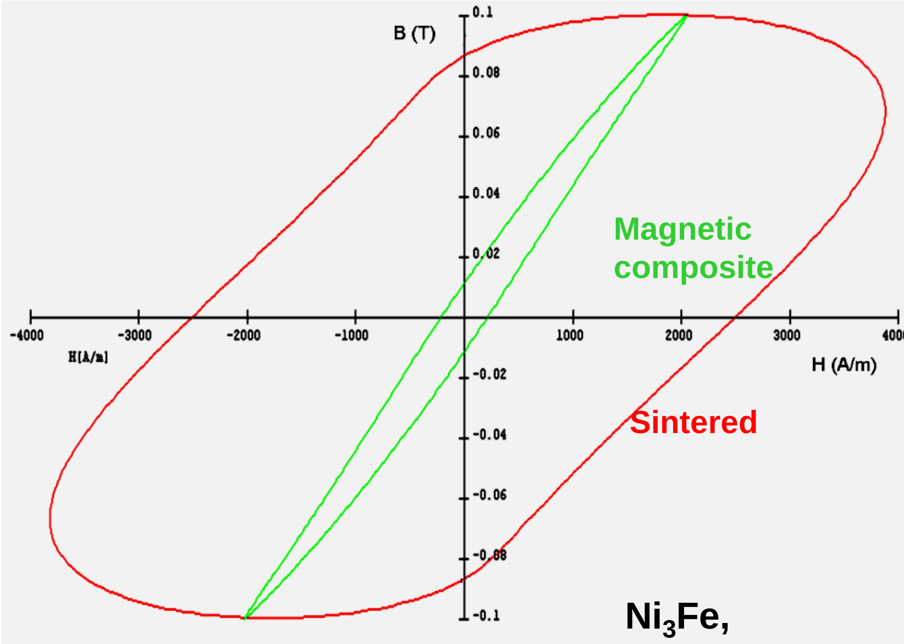
Outline

- Background and motivation
- Experimental details
- Results and discussion
  - Pseudo core-shell powders
  - Spark Plasma Sintered compacts
- Conclusions

Why composites materials?

Soft magnetic composites may open new range of applications extending the range of soft magnetic materials





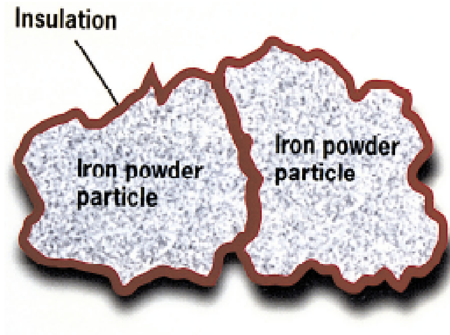
f = 10 kHz, B_{max} = 0,1 T

Ultimate aim is to produce soft magnetic nanocomposites

Background and Motivation

Classical SMC:

Fe-based magnetic alloys powders are covered with a thin dielectric organic/inorganic layer

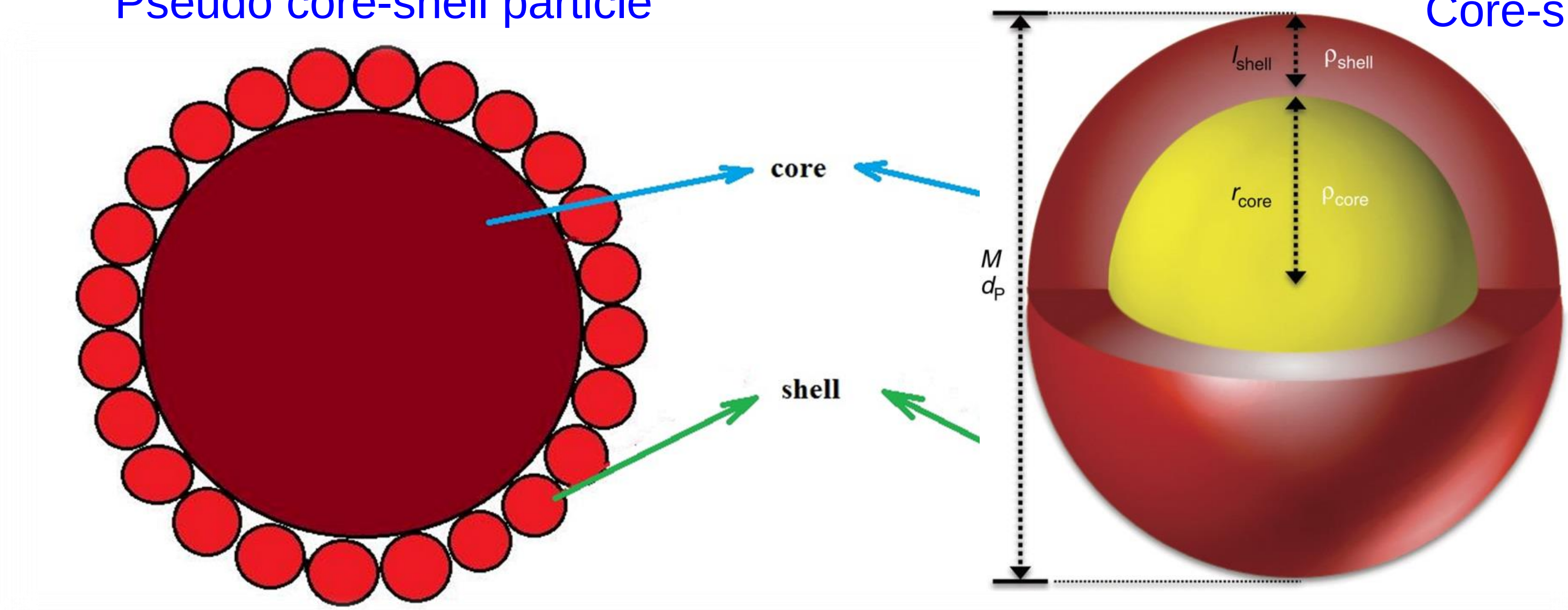


Effects: ρ ↗ M ↘

OUR IDEEA: to isolate magnetic particles by using a magnetic dielectric layer !
or amagnetic resistive alloy layer (Rhometal)!

Pseudo core-shell particle

Core-shell particle

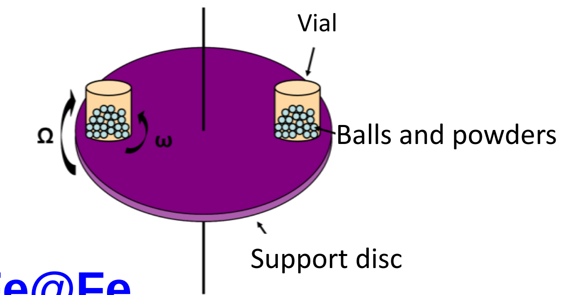


Experimental Details

Preparation

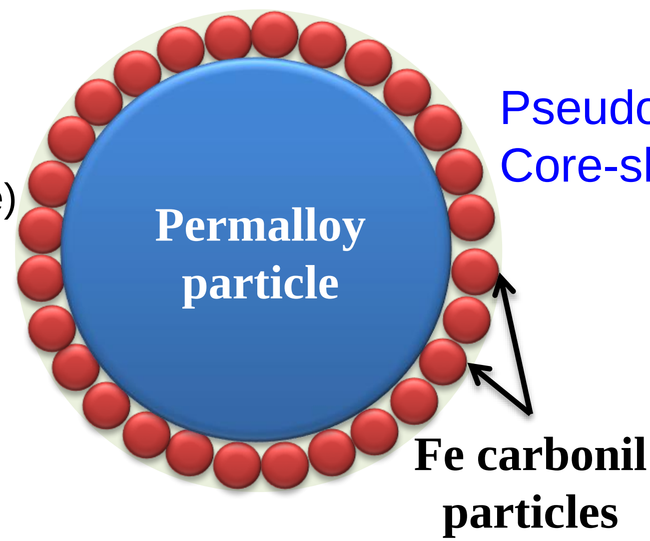
Nanocrystalline Ni_3Fe particles preparation

- Initial powder: Ni carbonyl and Fe NC100.24 (Höganäs)
- Mechanical alloying: Pulverisette 4 Fritch ball mill
- Milling time: 8 h



Pseudo ”core-shell” particles preparation Ni3Fe@Fe

- Initial powder: nanocrystalline Ni_3Fe + Fe NC100.24 (Höganäs) or Fe carbonyl (Sigma-Aldrich)
- Powder ratio: Ni_3Fe/Fe - 8.87/1.22 up to 6.95-3.05
- Homogenisation: Turbula type apparatus
  - Dry homogenisation
  - Wet homogenization (acetone)
- Compaction: 600 MPa
- Annealing: 400 and 900 °C for 1 h
- Post annealing: crushing and grinding



I. Chicinaş, T.F. Marinca, F. Popa, B.V. Neamţu, Patent RO 130354-B1/30.12.2016

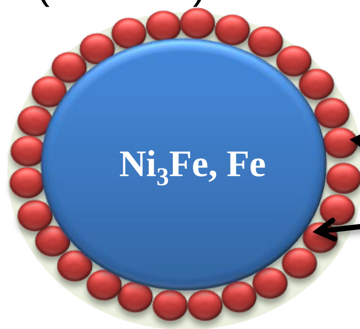
Preparation

Pseudo ”core-shell” particles preparation Fe-Ni alloys@$Ni_{1-x}Me_xFe_2O_4$

- Initial powders: nanosized $NiFe_2O_4$, $Ni_{0.5}Zn_{0.5}Fe_2O_4$, $Ni_{0.5}Cu_{0.5}Fe_2O_4$, $CuFe_2O_4$
  Fe NC100.24 (Höganäs) , d > 80 μm

Fe wt%	NiFe2O4 wt%	NiFe2O4 shell
96,1	3,9	2μm
94,2	5,8	3μm
92,49	7,51	4μm
90,65	9,35	5μm

- Homogenisation: Turbula type apparatus
  - dry homogenisation
  - wet homogenization (acetone)
- Annealing: 400 and 900 °C for 1 h
- Compaction: 600 MPa
- Post annealing: crushing and grinding



$Ni_{1-x}Me_xFe_2O_4$

compacts preparation

- Powder: pseudo ”core-shel” particles
  Permalloy@Rhometal
  Fe@$CuFe_2O_4$ and Ni-Fe alloy@$Ni_{1-x}Me_xFe_2O_4$
- Spark plasma sintering – SPS: pressure of 30 MPa and 400-900 °C temperature range, sintering duration 0 minutes (without maintaining)

Why SPS?

SPS home-made equipment

I. Chicinaş, T.F. Marinca, F. Popa, B.V. Neamţu, Patent application no. A/10083/2015/18.12.2015

Experimental Details

Caractérisation :

- **Particle size distribution** Laser Particle Size Analyser (Fritsch Analysette 22 – Nanotec)

- **Structural : X-ray diffraction** 2θ = 30 – 110 °, with Co Kα - INEL EQUINOX 3000
  in situ HT-X-ray diffraction

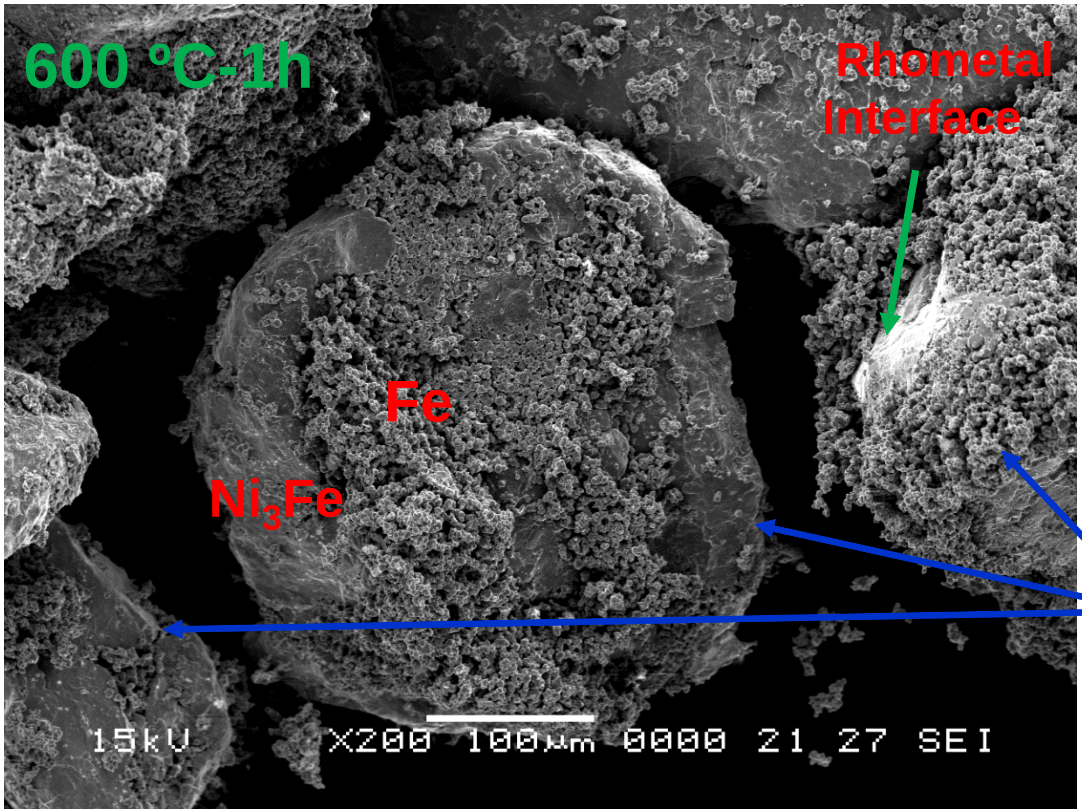
- **Morphology/composition - SEM and EDX:** (JSM 5600 LV-Jeol, EDX-Oxford Inst)

- **Magnetic measurements** : M = f(H) 0 – 8 T, 300 K , B=f(H) – cooperation with Université Grenoble Alpes, Institut NÉEL – CNRS

- **Electrical resistivity**

Pseudo ”core-shell” particles

Annealing of nanocrystalline Ni_3Fe and Fe carbonyl homogenized powder



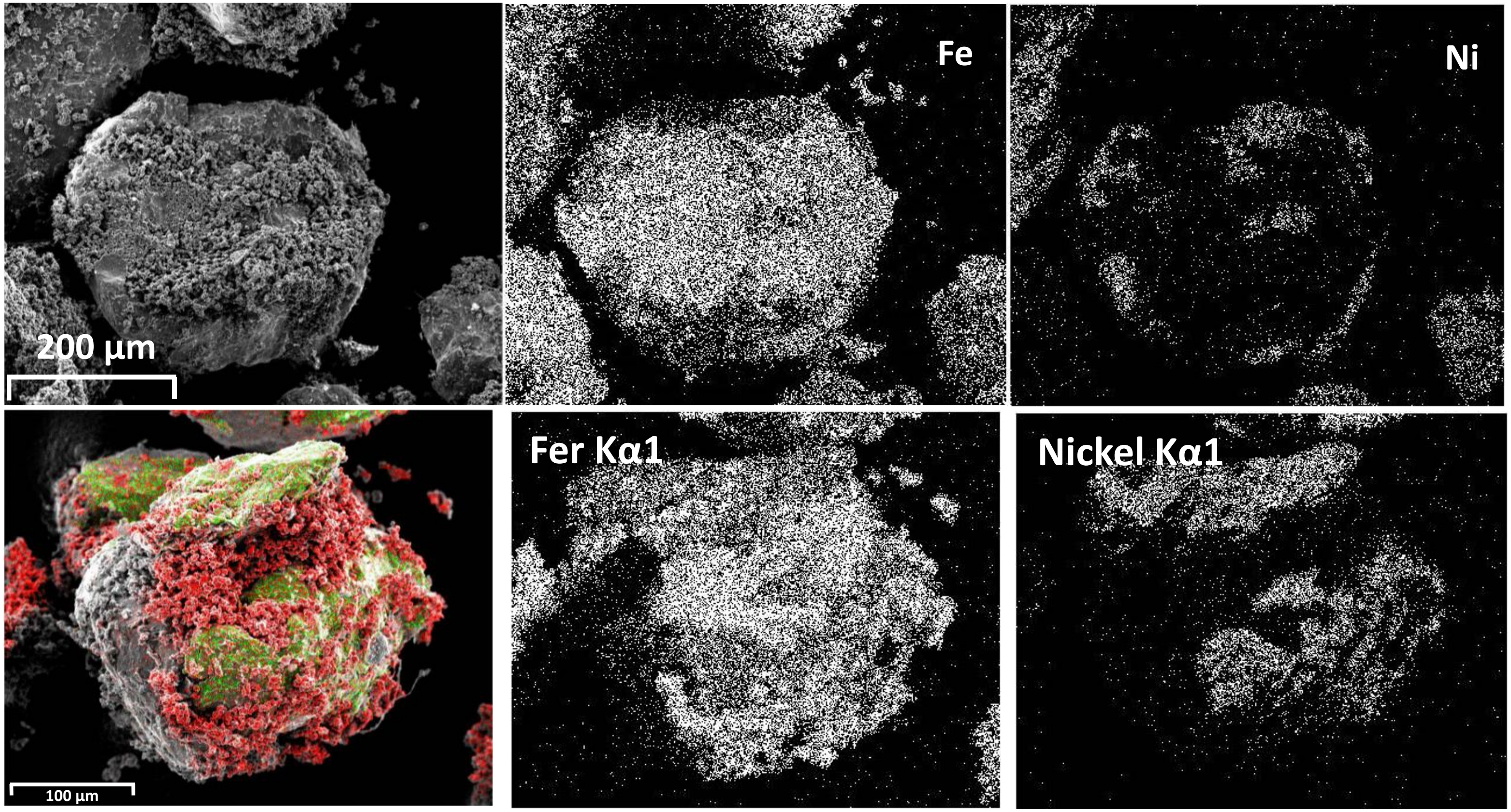
- Optimum annealing temperature – **600 ºC**
- pseudo **continuous** „shell”

Composite particles of **pseudo core-shell** type

EDX

Pseudo ”core-shell” particles

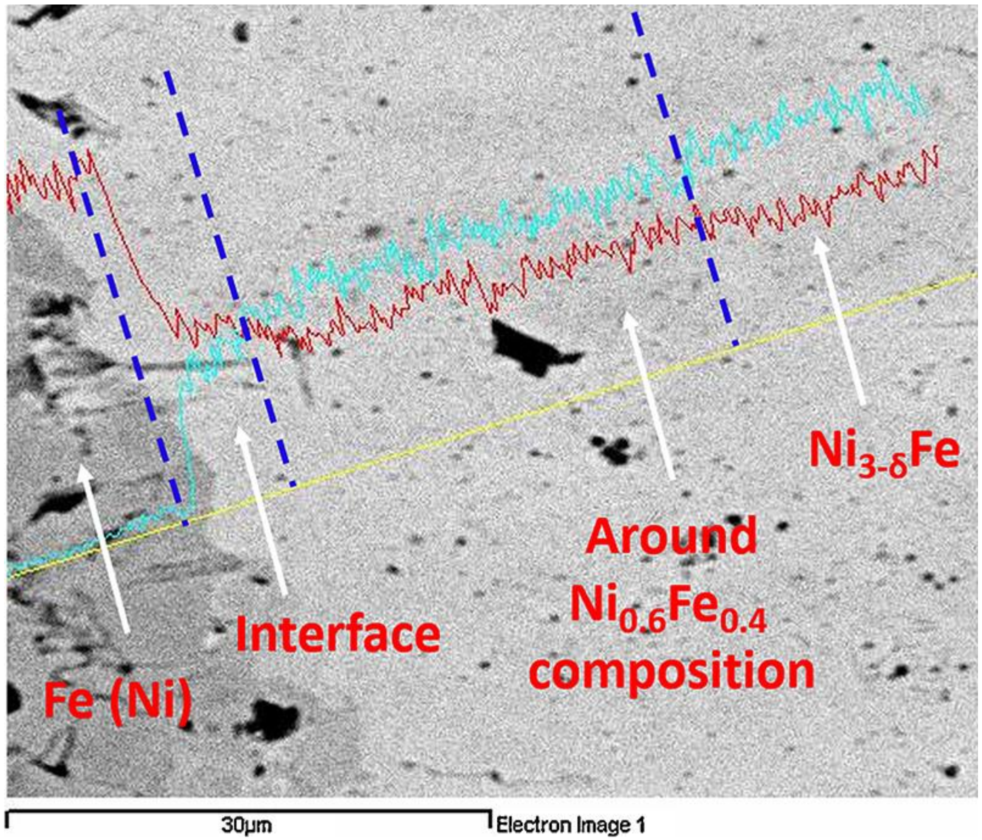
600 ºC-1h



- nanostructured particle is almost fully covered at the surface by a **layer of Fe**, Ni is almost inexistent in that zones.
- Ni is present in some zones, but there are a **limitet number of zones**.
- A **good covering** with an Fe layer.

I. Chicinas¸∗, T.F. Marinca, F. Popa, B.V. Neamtu, Appl. Surf. Sci. 358 (2015) 627–633

Sample Ni3Fe+ 17.9%Fe-carbonyl, 900 °C/1h



EDX line-scan analysis

4 zones in the composite particle:

1. $Ni_{3-\delta}Fe_{1+\delta}$
2. $Ni_{0.6}Fe_{0.4}$
3. Rhometal interface
4. Fe(Ni) alloy

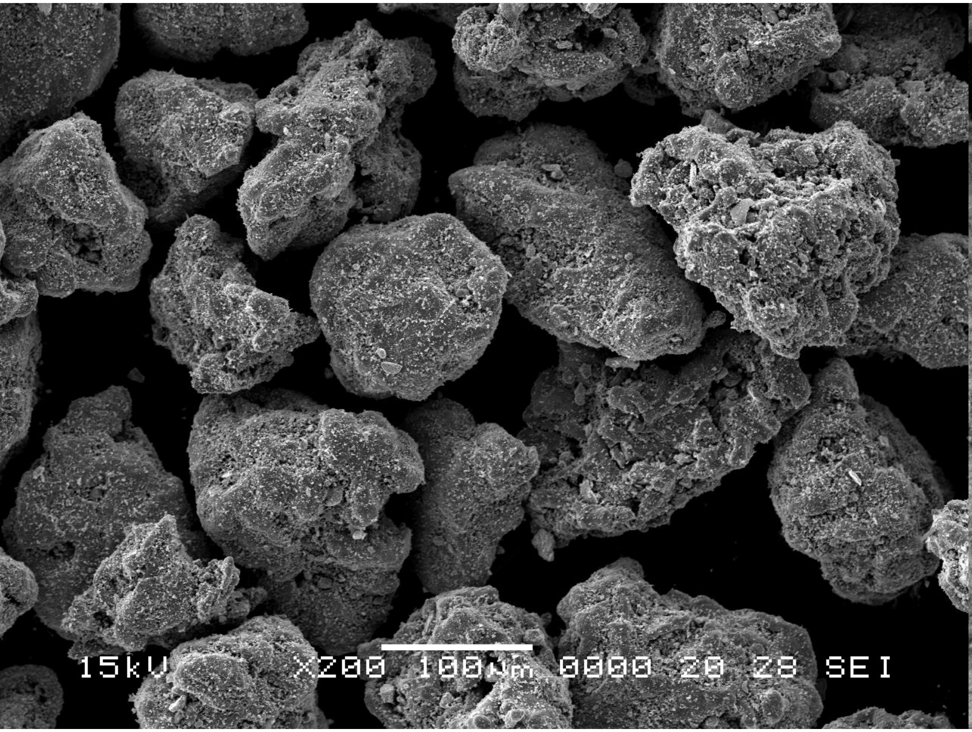
I. Chicinas¸∗, T.F. Marinca, F. Popa, B.V. Neamtu, Appl. Surf. Sci. 358 (2015) 627–633

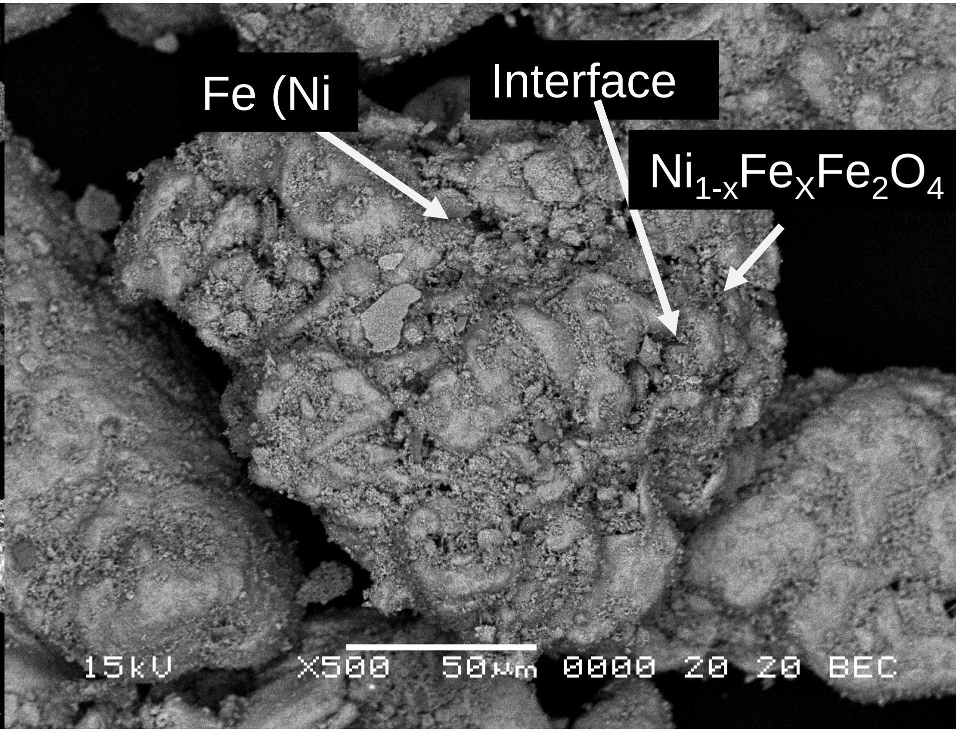
Results and discussion

Pseudo core-shell powder: $Fe@NiFe_2O_4$

7.5 wt% $NiFe_2O_4$ (d < 10 µm)
92.5 wt% Fe NC100.24 (d > 80 µm)

Wet mixing in acetone, 700 °C/1h





I. Chicinaş, T.F. Marinca, F. Popa, B.V. Neamţu, Patent application no. A/10083/2015/18.12.2015, OSIM

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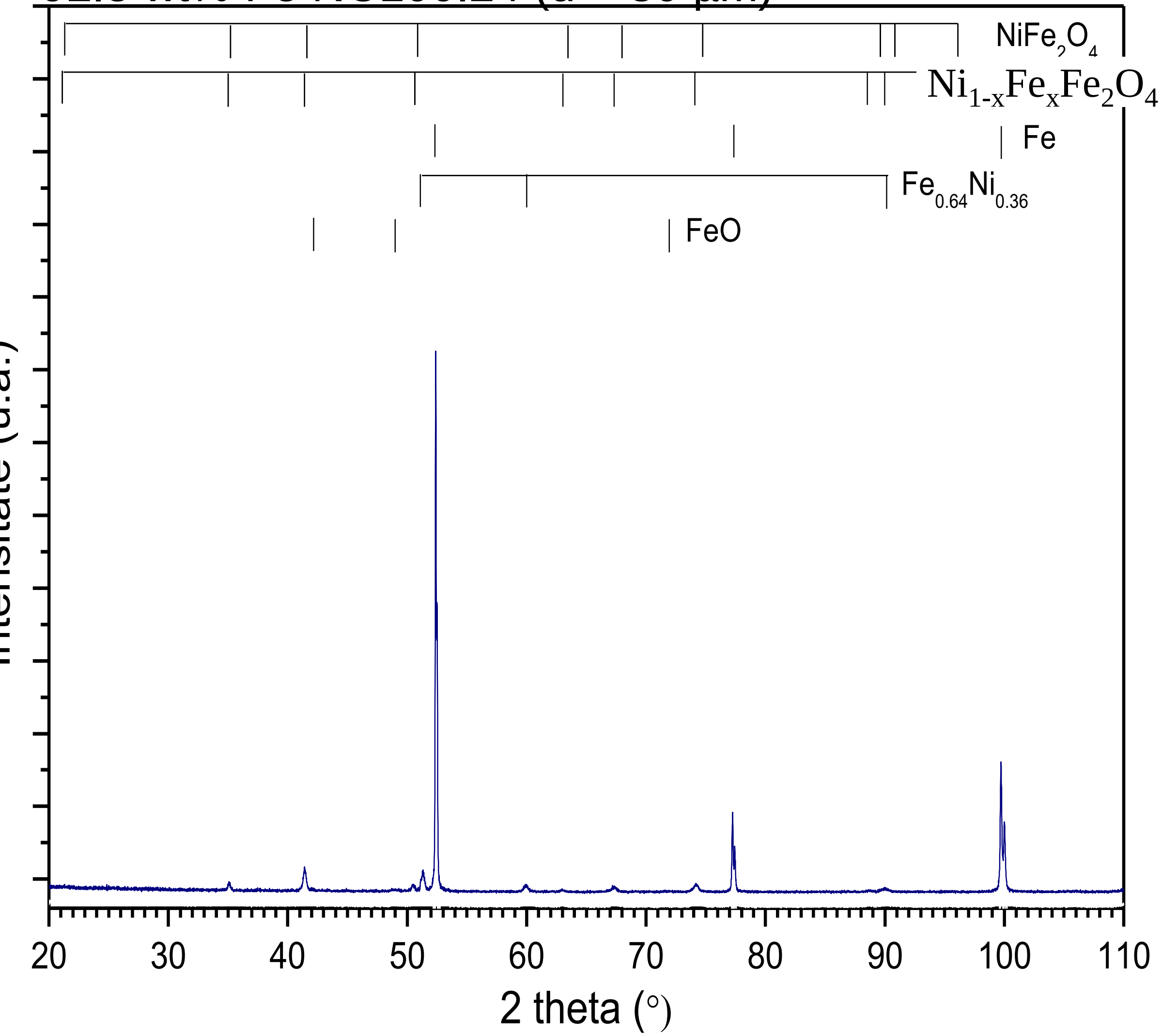


Interface forming by diffusion:

$NiFe_2O_4$
$Ni_{1-x}Fe_xFe_2O_4$
Fe64Ni36 phase (Rhometal)
FeO

$$NiFe_2O_4 + Fe \rightarrow Fe_3O_4 + Ni$$

$$xNi + (1 - x)Fe \rightarrow Fe_{1-x}Ni_x$$

$$FeFe_2O_4 + Fe \rightarrow 4FeO$$

I. Chicinaş, T.F. Marinca, F. Popa, B.V. Neamţu, Patent application no. A/10083/2015/18.12.2015, OSIM

SPS-ed compacts $Me@MeFe_2O_4$

$Ni_3Fe@Fe$

$Ni_3Fe@Ni_{0.5}Zn_{0.5}Fe_2O_4$

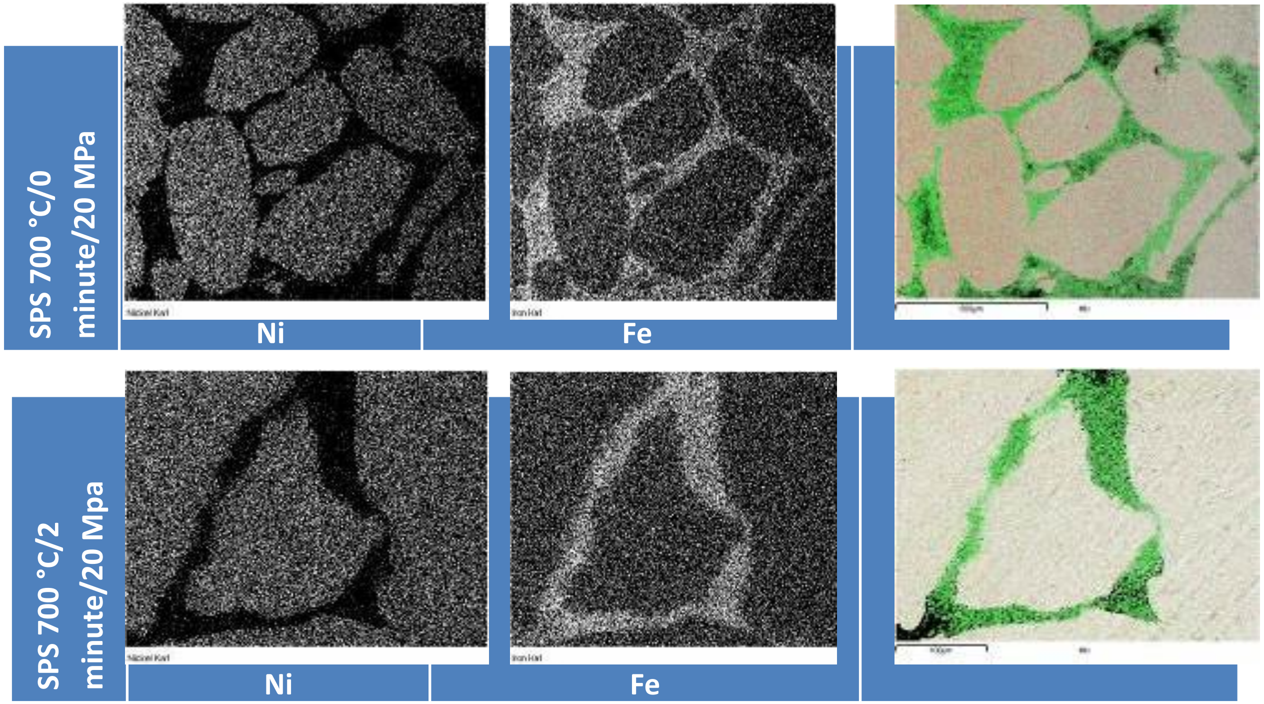
$Fe@CuFe_2O_4$

Results and discussion

SPS-ed compacts $Ni_3Fe@Fe$

Sample with 17.9 Fe

EDX analysis



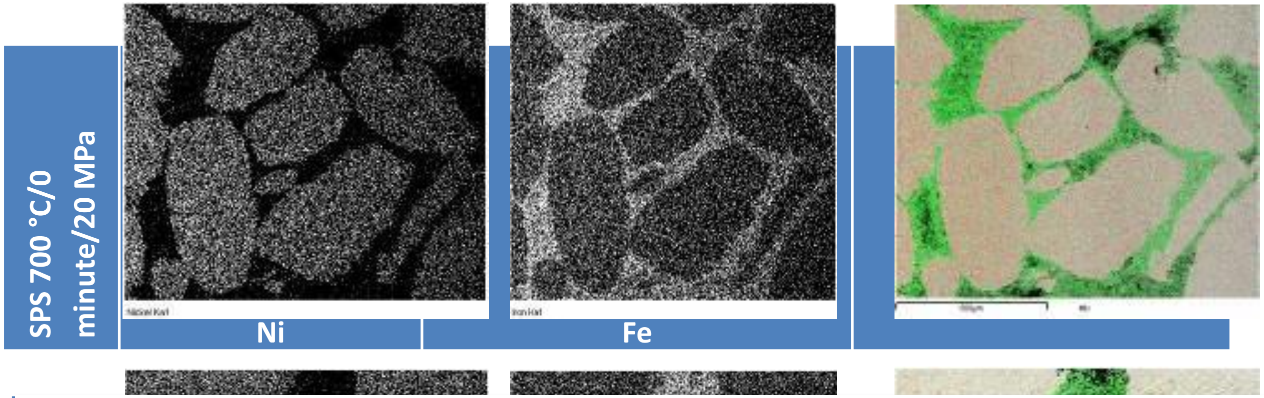
Composite compact:
Permalloy particles surrounded by a layer of Rhometal

-**Ni_3Fe clusters** in a **Fe matrix**
-**Ni** **missing** in matrix zone

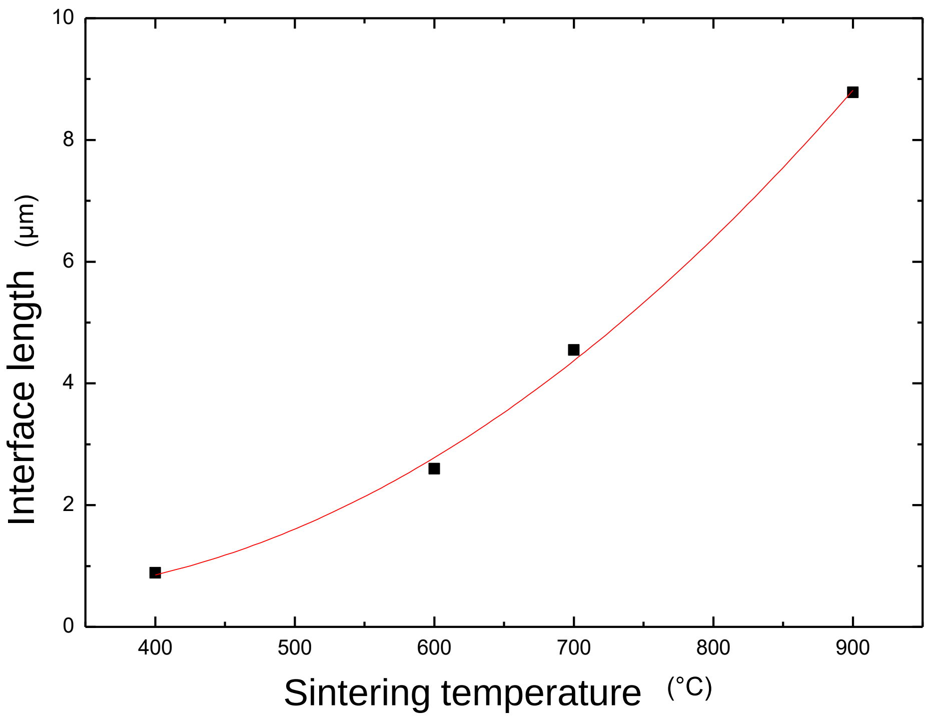
SPS-ed compacts $Ni_3Fe@Fe$

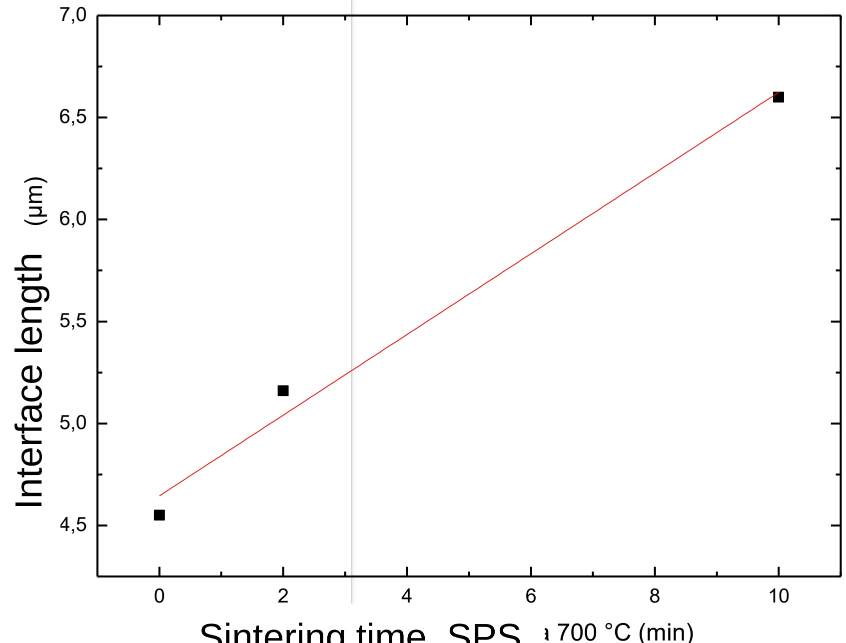
Sample with 17.9 Fe

EDX analysis

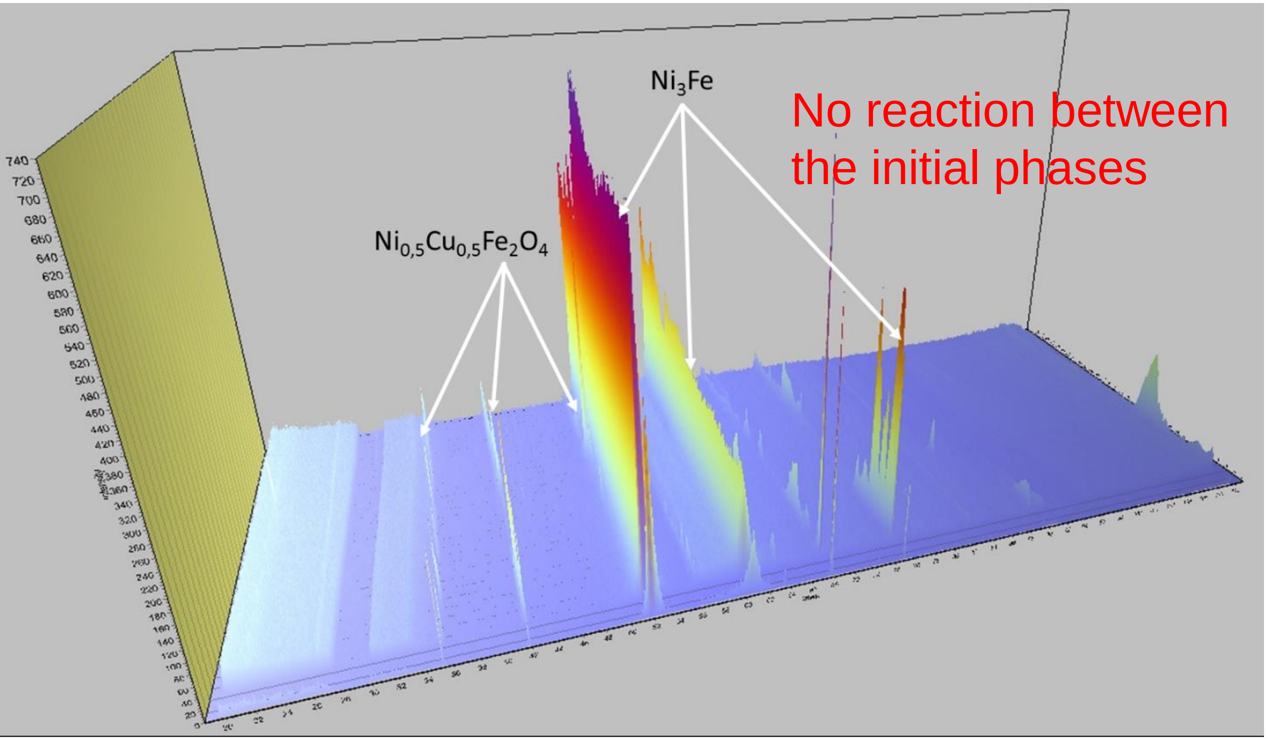


Composite compact:
Permalloy particles surrounded by a layer of Rhometal

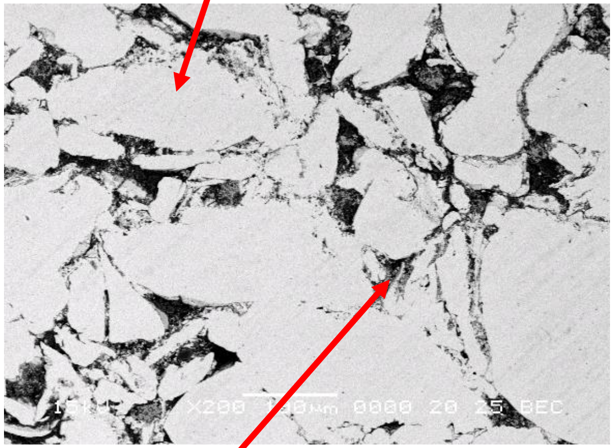




SPS-ed compacts $Ni_3Fe@Ni_{0.5}Zn_{0.5}Fe_2O_4$ (5μm)



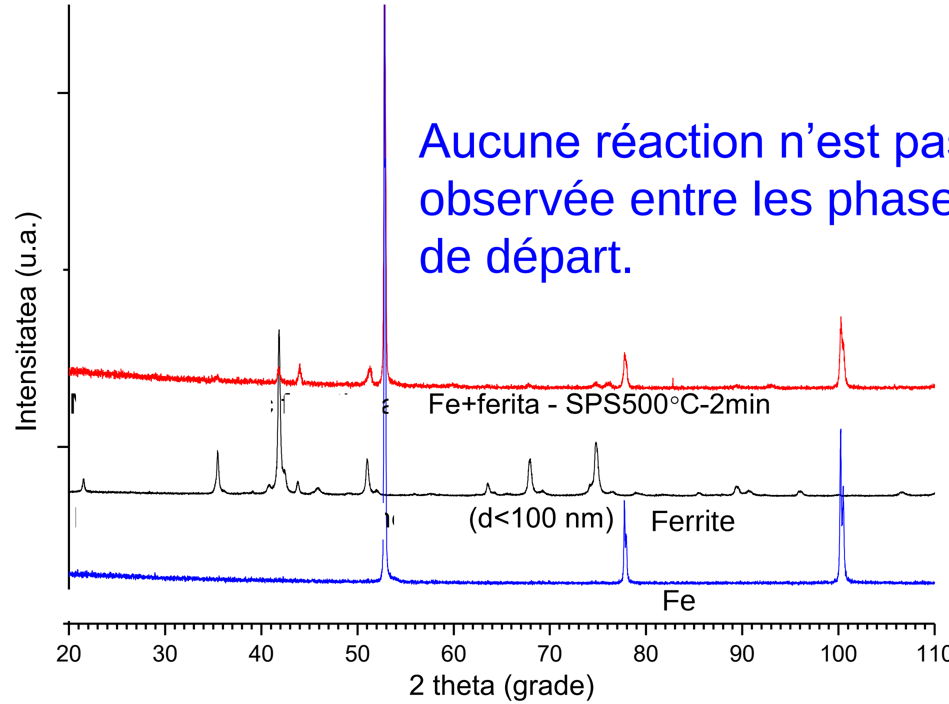
in situ HT-XRD analysis, temperature range: 20- 900 °C , $Ni_3Fe@Ni_{0.5}Zn_{0.5}Fe_2O_4$ (5μm)



SPS 600 °C-0 min

Compactes SPS $\underline{Fe@CuFe_2O_4}$ (5µm)

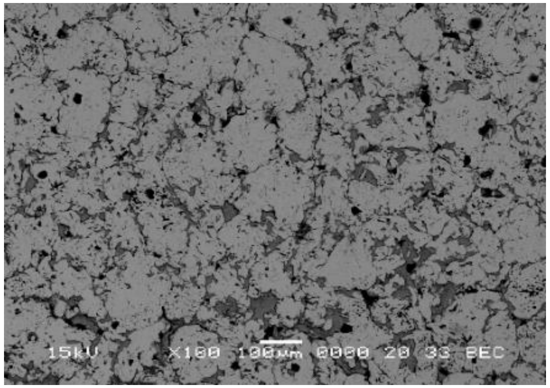
compactes SPS Fe@CuFe2O4

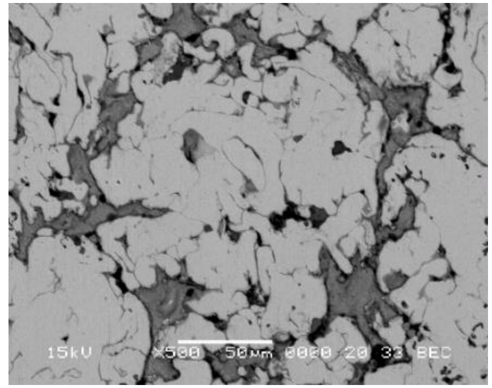


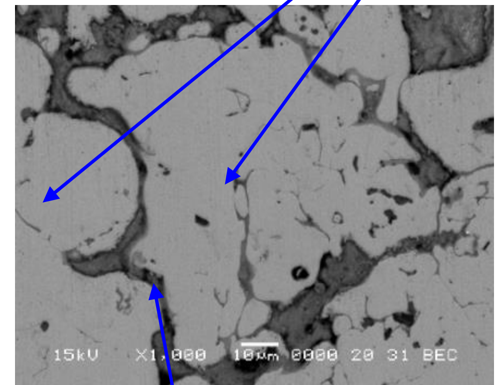
Aucune réaction n'est pas observée entre les phases de départ.

Diffractogrames XRD sur compates SPS Fe@CuFe2O4

Compactes SPS Fe/$CuFe_2O_4$ (5µm)

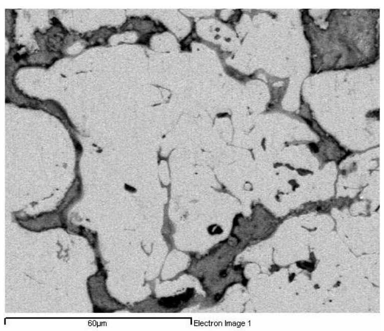


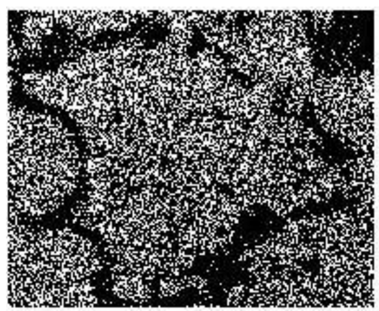


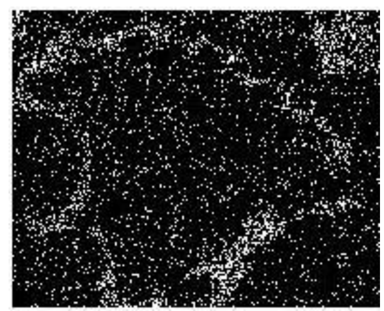


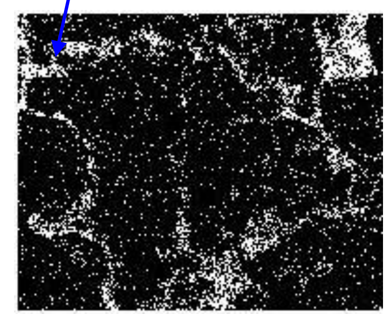
Images MEB sur le compactes SPS Fe/$CuFe_2O_4$, 500 °C, 2 min.

Microstructure de compact: des grandes particules de Fe dans un réseau diélectrique et magnétique de ferrite de Cu







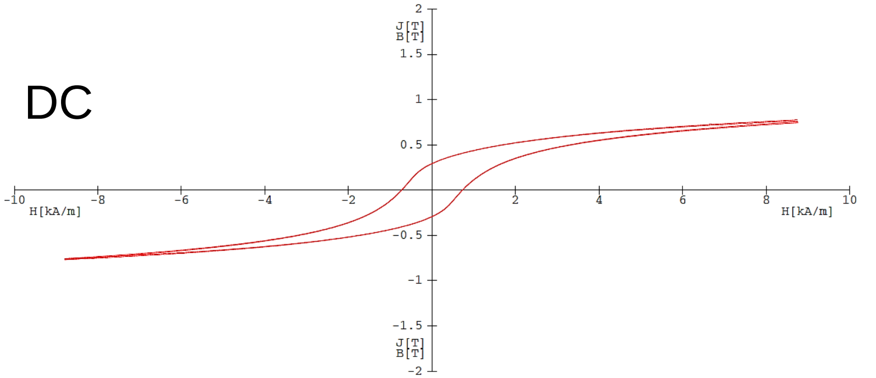


Cartes des distribution des éléments EDX sur les compactes SPS Fe/$CuFe_2O_4$, 500 °C, 2 min.

Compactes SPS $Fe/CuFe_2O_4$ (5µm)

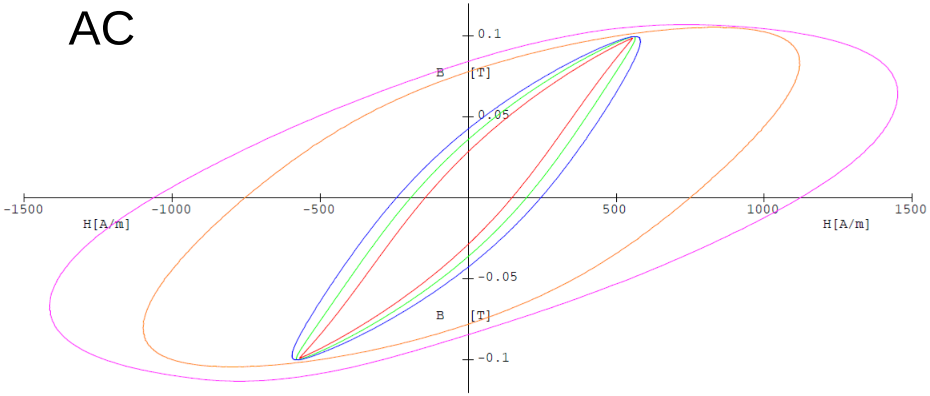
Propriétés magnétiques et électriques

DC



Br	=	0.293	T
HcB	=	727	A/m
HcJ	=	729	A/m
µrmax	=	175	
H(µrmax)	=		kA/m
Hmax	=	8.75	kA/m
Jmax	=	0.764	T
W	=	2.2	kJ/m³
T real	=	28.0	°C
T rated	=	28.0	°C
J(H1)	=	0.217	T
J(H2)	=	0.392	T

AC



		1	2	3	4	5	
f	=	50.0	500.0	1000.0	5000.0	10.0e3	Hz
Hmax	=	569.0	580.8	595.7	1450.6	1120.5	A/m
Bmax	=	0.099	0.1	0.1	0.11	0.105	T
Formf.B	=	1.102	1.111	1.110	1.114	1.107	
Br	=	0.029	0.036	0.043	0.084	0.078	T
Hc	=	146.6	195.4	243.5	1091.7	751.9	A/m
Ps	=	0.32	4.54	11.69	304.1	420.8	W/kg
µamp	=	140	138.8	135.1	61.18	75.21	

Perméabilité relative de 75 à B = 0,7 T et 10 kHz - est encourageant!

- ρ **≅ $1\cdot10^{-4}$ Ωm,** 3-4 ordre de grandeur supérieur à celui des alliages Fe-Si
- ρ **($6\cdot10^{-7}$ Ωm) –** en raison de la présence d'une **couche de ferrite**.

D'autres mesures électriques et magnétiques sont en cours…

Conclusions

- *The Permalloy(Supermalloy)@Rhometal pseudo core-shell powders were successfully obtained starting from nanocrystalline Ni_3Fe intermetallic compound and iron powder;*
- *The Ni-Fe Alloy@$Ni_{1-x}Me_xFe_2O_4$ pseudo core-shell powders were successfully obtained starting from Ni3Fe or Fe and $Ni_{1-x}Me_xFe_2O_4$ powders ;*
- *The core is composed by Permalloy or Fe and the shell consists in Fe-based alloy or in a soft magnetic ferrite layer;*
- *The Permalloy(Supermalloy)/Rhometal composite compacts has good magnetic properties*
- *The electrical resistivity of the SPS-ed composite compacts is with 3-4 order of magnitude larger than electrical resistivity of Fe-Si alloys*
- *SPS compacts have a larger electrical resistivity as compared to the Fe sintered compacts.*

Further investigations:

Pseudo core-shell Fe@ MnZnFe2O4 + SPS

Core-shell Fe@Fe304 + cold sintering

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