Ionel Chicinaş

Department of Materials Science and Technology, Technical University of Cluj-Napoca, Romania
Soft magnetic nanostructures

Small ferromagnetic crystallites coupled by exchange interaction

Local anisotropy Model

\[ D < L_{\text{ex}} \]

Local anisotropies are randomly averaged out by exchange interactions → there is not any anisotropy net effect on the magnetisation process

Low coercivity and high permeability

\[ H_C = p_c \frac{\langle K \rangle}{M_{\text{St}}} \approx p_c \frac{K_1^4}{M_{\text{St}} A_s^3} D^6 \]

\[ \mu_i = p_\mu \frac{M_{\text{St}}^2}{\mu_0 \langle K \rangle} \approx p_\mu \frac{M_{\text{St}}^2 A^3}{\mu_0 K_1^4} \cdot \frac{1}{D^6} \]


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Amorphous SM materials

partial crystallisation

Nanocrystalline soft magnetic materials

two-phase materials: nanocrystallites in an amorphous matrix

Mechanical routes for producing nanocrystalline powders

Mechanical alloying (MA) involves the synthesis of materials by high-energy milling.

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

$\Omega \rightarrow \omega \rightarrow$ shock mode process (SMP)

$\Omega \leftarrow \omega \rightarrow$ friction mode process (FMP)

Gibbs free energy per mole

\[ G^* \]
\[ \mu_A^0 \]
\[ \Delta G_M \]
\[ G\{x\} \]

Composition

A \hspace{1cm} x \hspace{1cm} B


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?

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

MAAC – can reduce the synthesis time!


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

\[ mA + nB = A_mB_n \]

\[ (1 - x) \cdot (mA + nB) + x \cdot A_mB_n = A_mB_n \]

Mechanical routes for producing of ferrites

- **Polycrystalline ferrite produced by solid state reaction (ceramic method)**
- **Stoichiometric mixture of oxides or of oxides and hidroxicarbonate**
- **Low temperature chemical coprecipitation (nanosized ferrite)**

**Mechanical milling** (dry or wet milling)

- **Mechanochemistry** (dry or wet milling)

- **Soft magnetic nanocrystalline (nanosized) ferrites**

- **MeFe$_2$O$_4$, Me = Mn, Cu, Zn, Ni**

- **≈80-95% spinel phase**

- **Annealing produces only spinel phase**

- **ZnFe$_2$O$_4$**

**References**

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Structural properties, phase composition

Partial reversibility during milling of the reaction:

\[ \alpha-\text{Fe}_2\text{O}_3 + \text{MeO} \leftrightarrow \text{MeFe}_2\text{O}_4 \]

The particles contain several related Fe–Me–O phases

Milling in closed vial:
\( \alpha-\text{Fe}_2\text{O}_3 \) is reduced at \( \text{Fe}_3\text{O}_4 \)

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

Particle size is generally reduced under 10 nm

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 saturate even in an applied field of 9 T.

The hysteresis loop is not symmetrical about the origin and is shifted to the left.

\[ \Delta H_C \] which increases with increasing the milling time.

Coexistence of both ferrimagnetic and superparamagnetic phase.
4.2 K

Ms decrease with milling time as a result of spin canting effect

Upon increasing milling time nanometer-sized CuFe$_2$O$_4$ particles decompose, forming $\alpha$-Fe$_2$O$_3$ – a further decrease of magnetisation

At higher milling time $\alpha$-Fe$_2$O$_3$ is reduced at Fe$_3$O$_4$ and $M_S$ increase

At 300 K a superparamagnetic behaviour in very small particles appears

Mechanical routes used for producing SMA

MA
- MM of oxides blend
- reduction of oxides
- alloying by heat treatment

MC*

MAAC

Two-step MA
- obtaining nanocrystalline alloy by MA

MAAC with inoculated germs
- obtaining nanocrystalline alloy by MM

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

## Soft magnetic nanocrystalline powder from Fe-Ni system

<table>
<thead>
<tr>
<th>Alloys Composition</th>
<th>Structure</th>
<th>Some magnetic properties</th>
<th>General Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>x$Ni$</em>{1-x}$, x = 7.69, 9.09, 11.11 at%</td>
<td>bcc and fcc phase mixture for x = 7.69 and 9.09 and only bcc phase for x = 11.11 at% [38]</td>
<td>Ni doping decreases the resonance frequency, but enhances the frequency stability [38]</td>
<td>38</td>
</tr>
<tr>
<td>Fe-10 wt% Ni</td>
<td>bcc solid solution [21]</td>
<td>$H_C = 200A/m$ after 96 h milling [30]; $H_C = 1600 A/m$ for shock power mode milling conditions [32]</td>
<td>21, 30-33, 40</td>
</tr>
<tr>
<td>Fe-15 wt% Ni</td>
<td>bcc solid solution [46]</td>
<td>high value of complex permeability in 1-10 GHz [46];</td>
<td>46</td>
</tr>
<tr>
<td>Fe-20 wt% Ni</td>
<td>α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) [34] bcc phase [21]</td>
<td>$M_s = 219 Am^2/kg$ [30]; $H_C = 110A/m$ after 96 h milling [30]; $H_C = 1420 A/m$ for shock power mode milling conditions [32]</td>
<td>19, 21, 24, 30-34, 40</td>
</tr>
<tr>
<td>Fe-25 wt% Ni</td>
<td>α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) [34]</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Fe-30 wt% Ni</td>
<td>α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) [26, 34]</td>
<td></td>
<td>26, 34</td>
</tr>
<tr>
<td>Fe-35 wt% Ni</td>
<td>α-Fe(bcc) + Ni(fcc) → α'-Fe(bct) → γ(fcc) [34] final structure α'-Fe(bct) + γ(fcc) [26]</td>
<td>Invar anomaly for 35 at% was not detected [24]; larger $T_C$ than that for equilibrium alloys [24];</td>
<td>19, 24, 26, 31, 34</td>
</tr>
<tr>
<td>Fe-50 at% Ni Fe-50 wt% Ni</td>
<td>γ (fcc) after 22 h [24]</td>
<td>larger $T_C$ than that for equilibrium alloys [24];</td>
<td>15, 19, 24, 31, 37</td>
</tr>
<tr>
<td>Ni$_3$Fe</td>
<td>cfc, disordering by milling time [24]</td>
<td>$H_C=800A/m$ pt D = 11 nm [20]; $H_C$ increases with increase milling time [22]; there is a fall in the $M_s$ for the 70h milling due to the presence of super paramagnetic particles [25]; $M_s$ decreases at milling time longer than 20 h, due to presence of anti-site disorder [29,41,42].</td>
<td>15, 20, 22, 23, 25, 28, 29, 41 - 43</td>
</tr>
</tbody>
</table>
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.


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.


Influence of the milling intensities on the magnetic properties and of the structure and local atomic order of Ni atoms was observed in both two processes.


Ni₃Fe phase formation

• first order internal stresses

peaks shift to LOWER 20 angles

Peaks shift to HIGHER 20 angles

Relax the first order internal stresses

Annealing effect

Improve the solid state reaction

2θ (°)

Ni$_3$Fe produced by MAAC

One annealing time Different milling time

One milling time Different annealing time

\[ d = \frac{k \cdot \lambda}{\beta_{1/2} \cdot \cos \theta} \]

\[ \beta_{1/2} \text{ - FWHM} \]

\[ d = \begin{cases} 
12 \text{ nm} & \text{52 h milling} \\
22 \text{ nm} & \text{24 h milling}
\end{cases} \]

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

Fe$_{1-x}$Ni$_x$ in the reach nickel region*

I. Chicinas, V. Pop and O. Isnard,

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


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Ni3Fe produced by MAAC

Influence of the milling and annealing conditions on the $M_s$

V. Pop, O. Isnard and I. Chicinas,
Ni$_3$Fe produced by MAAC

Influence of the milling and annealing conditions on the $M_s$

![Graph showing the influence of milling and annealing conditions on $M_s$](image)

$T = 330 \, ^\circ C$


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Mössbauer spectrometry
Ni$_3$Fe powders

Mechanical Alloying and Annealing Combining technique

Milling – Annealing - Transformation (MAT) diagram

Nanocrystalline soft magnetic powders from Fe-Ni-X systems

FeNi\(3)x\Ag1-x, \ Nic50Al50-x\Fetch, \ Fe49\Nic46\Moc5, \ Fe42\Nic40\B18, \ Ni-15%\Fe-5%\Moc \ and \ Ni-16%\Fe-5%\Moc \ (wt\%) \ and \ others

The presence of Ag in (FeNi\(3)x\Ag1-x \ alloys increasing the coercive field as compared to the value of Ni3Fe.

Both Mo and B have a dramatic effect on the MA process and magnetic properties of Fe-Ni-based materials, mainly by changing the thermodynamic and kinetics of amorphsation and nanocrystal formation.
Supermalloy synthesis by MAAC:
- 8 hours milling
- different annealing conditions.

\[ d = \frac{k \cdot \lambda}{\beta_{1/2} \cdot \cos \theta} \]
\[ \beta_{1/2} - \text{FWHM} \]

8 hours milling

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

the mechanical alloying process occurs in two steps
an intermediate amorphous or poorly crystallized phase, (Ni,Fe)–Mo type.

Y. Shen, H.H. Hng, J.T. Oh,

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. Chicinaș,
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 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.

**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.
Soft magnetic nanocrystalline composites

Composites Production

polymer dissolving Ni$_3$Fe nano covered powder (1, 1.5, 2, 3 wt%) → polymer layer → Ni$_3$Fe

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

Conclusions

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.
Acknowledgements

- **Prof. Olivier Isnard**, Laboratoire de Cristallographie, CNRS, associé à l'Université J. Fourier, Grenoble, France
- **Prof. Viorel Pop**, Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania
- **Prof. Jean Marie Le Breton**, Groupe de Physique des Matériaux, UMR CNRS 6634, Université de Rouen, France
- **Prof. Zeno Sparchez**, Department of Materials Science and Technology, Technical University of Cluj-Napoca, Romania
- **Prof. Olivier Geoffroy**, Laboratoire Louis Neel, CNRS, associé à l'Université J. Fourier, Grenoble, France

Thanks for your attention!