Effect of Milling and Annealing Conditions on the Interphase Exchange Coupling of \( \text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe} \) Magnetic Nanocomposites

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Outline

• Introduction
• Experimental details
• Structure and microstructure
• Inter-phase magnetic coupling
• Conclusions
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Nanophased materials behave differently from their macroscopic counterparts because their characteristic sizes are smaller than the characteristic length scales of physical phenomena occurring in bulk materials.

\[ l_{sc} = \sqrt{\frac{2A_{sc}}{\mu_0 M_s^2}} \]

\[ l_{sc} \sim 3 - 7 \text{ nm} \]

\[ \delta = \pi \sqrt{\frac{A}{K}} \]

\[ \delta \sim 30 \text{ nm} \]

\[ N_{d}Fe_{14}B : \delta \sim 5 \text{ nm} \]

\[ \delta \sim 4 - 100 \text{ nm} \]

Fe : \[ \delta \sim 30 \text{ nm} \]

Nd_{2}Fe_{14}B : \[ \delta \sim 5 \text{ nm} \]

Magnetocrystalline anisotropy

Energy dependent of \( \theta \)

Magnetic configuration in magnetic nanostructures: domains, walls, vortex, configuration magnetic anisotropy, etc

Theoretical predictions:

- Best magnets on the market: 
  \((BH)_{\text{max}} \approx 500 \text{ kJ/m}^3\)

- \((BH)_{\text{max}} = 1090 \text{ kJ/m}^3\) for nanostructured multilayers \(\text{Sm}_2\text{Fe}_{17}\text{N}_3/\text{Fe}_{65}\text{Co}_{35}\)


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

Kronmuller & Coey *Magnetic Materials*, in *European White book on Fundamentel Research in Materials Science* 
high anisotropy
+
large magnetization

exchange

hard phase

soft phase

Exchange spring magnets
Structure Microstructure $\rightarrow$ Soft-hard exchange hardness

- High anisotropy
- Large magnetization

- Hard phase
- Soft phase

Exchange

Exchange spring magnets

$D_{cr} \geq 2h$

$\delta_h = \pi \sqrt{A_h / K_h}$

$D_{cr} =$ soft phase critical dimension

$\delta_h =$ width of domain wall in the hard phase

$A_h$ and $K_h$ are the exchange and anisotropy constants
Nanocomposites prepared by mechanical milling (MM)

- hard magnetic phases of $\text{Nd}_2\text{Fe}_{14}\text{B}$
- soft magnetic phases of $\alpha$-Fe (10 wt%)

Different milling energy:
1. Different milling balls: $\Phi$ 10 mm and 15 mm
2. Different milling time: 6 h and 8 h of MM
Nanocomposites prepared by mechanical milling (MM)

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Milling energy

Size of $\alpha$-Fe crystallites

Crystallinity of the hard phase

Size of $\alpha$-Fe crystallites

Interphase exchange coupling

Crystallinity of the hard phase
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Material preparation

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

Starting materials:

- hard magnetic phases of: 
  \( R_2Fe_{14}B, \text{ ingots} \) – prepared by melting
- soft magnetic phases of: 
  Fe NC 100.24 powder (Höganäs), (< 40 μm)

Mechanical milling experiments:

- hard magnetic phases – crushed under 500 μm
- hard + soft magnetic powders – milled in Ar atmosphere for 2 – 8 h

Annealing:

- short time annealing: in argon/700, 750 or 800 °C for 0.5 to 3 min.
By Mössbauer spectroscopy we detected an inter-diffusion between the two phases during milling or annealing.*

Some previous studies:

Some previous studies:

Atom probe tomography (APT) suggested that the observed Fe/Co inter-diffusion is initiated during the milling process and further increased by the annealing treatments.*

Nanoscale analysis of the SmCo$_5$/Fe powder milled for 8h:
(a) 3D image of Fe-rich clusters
(b) Concentration profile through a Fe-rich cluster along the black dashed arrow in panel (a).

Material characterisation

- X-ray diffraction (XRD)
- DSC measurements
- Magnetic measurements
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- The milled powders present poor crystallinity and a high defect density.

- The recrystallization temperature of the soft magnetic phase is smaller than the recrystallization temperature of the hard magnetic phases.

- By annealing we intended to recover the crystallinity of the hard phase and, in the same time, to hinder the growth of Fe crystallites during annealing.

- In order to complete both objectives simultaneously, a good crystallinity for the hard phase and fine crystallite (smaller than 20 nm) for Fe phase, we also investigate the effects of short time annealing (0.5 to 3 min at 700, 750 and 800 °C) on the structure, microstructure, and magnetic properties of the hard/soft Nd$_2$Fe$_{14}$B/α-Fe magnetic composite.
Classical annealing
(450-650 °C for 0.5 up to 10 h)

Short time annealing
(700, 750 or 800 °C for 0.5 to 3 min)

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Annealing time (min)</th>
<th>FWHM (°)</th>
<th>D (nm) α-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1.0</td>
<td>0.88</td>
<td>12 (±2)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.77</td>
<td>14 (±2)</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.66</td>
<td>16 (±2)</td>
</tr>
<tr>
<td>800</td>
<td>1.0</td>
<td>0.61</td>
<td>17 (±2)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.50</td>
<td>21 (±2)</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.43</td>
<td>25 (±2)</td>
</tr>
<tr>
<td>550</td>
<td>90</td>
<td>0.40</td>
<td>26 (±2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Annealing time (min)</th>
<th>D (nm) α-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1.0</td>
<td>15 (±2)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>19 (±2)</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>24 (±2)</td>
</tr>
<tr>
<td>750</td>
<td>1.0</td>
<td>19 (±2)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>22 (±2)</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>28 (±2)</td>
</tr>
<tr>
<td>800</td>
<td>1.0</td>
<td>24 (±2)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>27 (±2)</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>30 (±2)</td>
</tr>
<tr>
<td>450</td>
<td>90</td>
<td>14 (±2)</td>
</tr>
<tr>
<td>550</td>
<td>90</td>
<td>26 (±2)</td>
</tr>
<tr>
<td>650</td>
<td>90</td>
<td>38 (±2)</td>
</tr>
</tbody>
</table>

Nd$_2$Fe$_{14}$B + 22% α-Fe


Nd$_2$Fe$_{14}$B + 10% α-Fe

8h MM

Different diameters of the milling balls

Different energy of milling
Different diameters of the milling balls

Different energy of milling

<table>
<thead>
<tr>
<th>Milling time (h)</th>
<th>Annealing temperature (°C)</th>
<th>Annealing time (min)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 (Ø 10 mm)</td>
<td>700</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2.5</td>
<td>20</td>
</tr>
<tr>
<td>6 (Ø 15 mm)</td>
<td>700</td>
<td>2</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>2.5</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>550 [10]</td>
<td>90</td>
<td>34</td>
</tr>
<tr>
<td>8 [7]</td>
<td>700</td>
<td>1.5</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.5</td>
<td>26</td>
</tr>
</tbody>
</table>


Different times of milling

Different energy of milling

Better crystallinity for 6 h MM
Different times of milling

Different energy of milling

Smaller crystallites for 8 h MM
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high anisotropy + large magnetization → hard phase ↔ exchange ↔ soft phase → Exchange spring magnets

Diagram:
- M vs. H
- Blue line: Hard - soft exchange coupled
- Green line: Hard - soft uncoupled
The filled and empty symbols correspond to the samples milled with Ø 10 mm and Ø 15 mm balls respectively.

The better crystallinity of the hard magnetic phase (for the less energetic MM) impose a better coupling.

<table>
<thead>
<tr>
<th>Milling time (h)</th>
<th>Annealing temperature (°C)</th>
<th>Annealing time (min)</th>
<th>d (nm)</th>
<th>$\mu_0 H_c$ (T)</th>
<th>$M_r$ (Am$^2$/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 (Ø 10 mm)</td>
<td>700</td>
<td>1.5</td>
<td>10</td>
<td>0.42</td>
<td>114</td>
</tr>
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<td></td>
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<td>15</td>
<td>0.44</td>
<td>114</td>
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<tr>
<td></td>
<td></td>
<td>2</td>
<td>20</td>
<td>0.38</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2.5</td>
<td>21</td>
<td>0.41</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>25</td>
<td>0.17</td>
<td>97</td>
</tr>
<tr>
<td>6 (Ø 15 mm)</td>
<td>700</td>
<td>2</td>
<td>17</td>
<td>0.48</td>
<td>114</td>
</tr>
<tr>
<td>750</td>
<td>2.5</td>
<td>20</td>
<td>0.41</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>2</td>
<td>16</td>
<td>0.51</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>550 [10]</td>
<td>90</td>
<td>34</td>
<td>0.55</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>1.5</td>
<td>16</td>
<td>0.51</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>8 [7]</td>
<td>800</td>
<td>26</td>
<td>0.54</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>
Higher coercivity for the 6h MM samples

Better Nd$_2$Fe$_{14}$B crystallinity

Lower milling energy

Higher milling energy

More Fe present due to Nd$_2$Fe$_{14}$B decomposition during milling

Slightly higher remanence for 8h MM
Different times of milling = Different energy of milling

Best exchange coupling for 6h MM + 750°C
Conclusions

- The structure and microstructure have a strong influence on the hard/soft exchange coupling.
- The crystallinity and the anisotropy of hard magnetic phases are strongly influenced by milling.
- The characteristic diffractions peaks of hard magnetic phases are restored during heat treatment. The annealing induces also a refinement of the soft magnetic phase structure.
- Lower milling energies increase the coercive field due to a reduced damaging of the hard phase crystal structure.
- Higher milling energies lead to a slight remanence increase due to a higher percentage of Fe present in the milled samples resulting from the Nd$_2$Fe$_{14}$B decomposition during milling.
- The hard/soft interphase exchange coupling is more sensitive to the crystallinity of hard phase than to the small variations of the crystallite size of soft phase.
Thank you for your attention

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