The Nd$_2$Fe$_{14}$B/$\alpha$-Fe nanocomposites were obtained by recrystallisation from an amorphous phase, prepared by melt spinning. For all Fe contents, between 83 and 89 at.%, we have obtained the hardening of the $\alpha$-Fe phase by exchange interactions between the hard Nd$_2$Fe$_{14}$B phase and the soft $\alpha$-Fe phase. For all isotropic permanent magnets obtained from the prepared nanocomposites, we measured remanence ratio higher than 0.6, which confirm the existence of the mentioned exchange interactions. The impossibility to control the recrystallisation performs to a large distribution of the grain sizes of the $\alpha$-Fe phase and determines a significant decrease of the magnetic performances. The analysis of the interactions between the hard and the soft phases shows that this decrease is impossible to be avoided in our NdFeB nanocomposites.

1. INTRODUCTION

Kneller and Hawig [1] recognized the possibility to harden through exchange interactions two-phase nanostructures, composed by a hard magnetic phase and a soft ferromagnetic phase. Such isotropic nanocomposites show a behaviour like anisotropic permanent magnets, having the relative remanence for this so-called spring magnets, $M_r / M_S > 0.5$. Shomski [2, 3] has showed that such aligned nanocomposites from the type Nd$_2$Fe$_{14}$/ $\alpha$-Fe can have very high energy densities.

Schrefl et al. [4, 5] analyzed through numerical computation the dependence of the magnetic properties of Nd$_2$Fe$_{14}$B/$\alpha$-Fe nanocomposites from the dimensions and concentration of $\alpha$-Fe inclusions. They have found a decrease of the coercivity with the $\alpha$-Fe content and a sharp deterioration of the magnetic properties, if the grain sizes of the $\alpha$-Fe phase exceed 20 nm.

Zern et al. [6] show, that the intrinsic coercivity, done by

$$\Delta H_C(T) = \alpha_K \alpha_{ex} H_A - N_{eff} M_S,$$

where $H_A$ is the anisotropy field, $N_{\text{eff}}$ the effective local demagnetizing factor, $M_S$ is the saturation magnetisation, $\alpha_K$ the local reduction of the anisotropy, $\alpha_{\text{ex}}$ the reduction of the coercivity done by exchange interactions between the grains, is reduced by a factor of $1/3$ with $\alpha$-Fe additions ranging from 0% to 40%.

For an assembly of nanoparticles with crystal and shape anisotropy, Schmidt and Ram [7] developed a micromagnetic model to calculate the nucleation field of such a system.

Exchange spring magnets can be prepared by various methods, like mechanical alloying, rapid quenching with short – time annealing [8], spark plasma-sintering [9]. In order to enhance the magnetic properties, different rare earth substitutions [10, 11] and microalloying elements have been used [12].

Lewis et al. [13] studied the influence of the stresses in the $\alpha$-Fe inclusions on the magnetic properties of Nd$_2$Fe$_{14}$B/$\alpha$-Fe composites.

The effect of the grain size and magnetocrystalline anisotropy on the exchange hardened NdFeB/$\alpha$-Fe nanocomposites was studied by Xiao et al. [14], who has been found, in accordance with [4], a sharp decrease of the magnetic properties in Nd$_4$Fe$_{77.5}$B$_{18.5}$ if the grain size of the soft Fe$_3$B increase over 20 nm.

Yang et al. [15] showed, in a spherical two layer model, that the critical radius for the grain size of the soft $\alpha$-Fe phase must be:

$$R_C = \sqrt{M_h A_s / K_h M_s}$$

where $M_h$, $M_S$ and $K_h$, $A_S$ are respectively the magnetisations, the anisotropy constant and exchange constant of hard (h) and soft (s) phases. At $R < R_c$ the nucleation field is constant and for $R > R_c$ a strong reduction of the coercivity can be observed in two phase nanocomposites.

Generally, it is deduced that the critical diameter of the soft grains must be twice the width of the domain wall of the hard magnetic phase [13], which is for Nd$_2$Fe$_{14}$B around 50 Å.

The aim of our work was to analyze the dependence of the coercivity of Nd$_2$Fe$_{14}$B/$\alpha$-Fe composites from the $\alpha$-Fe content, to analyze the contributions to the spring effect of soft $\alpha$-Fe inclusions in the hard magnetic phase, and, if possible, to establish, an upper limit of the $\alpha$-Fe inclusions.

2. EXPERIMENTAL DETAILS

The NdFeB alloys were prepared by melting in a vacuum induction furnace [16], starting from Fe80Nd20, Fe20B80 master-alloys and technical pure iron, with compositions beginning from Nd$_2$Fe$_{14}$B + 5 wt.% Fe up to 35 wt.% Fe (Table 1).
Table 1

Chemical compositions of melt spun NdFeB ribbons

<table>
<thead>
<tr>
<th>Cod sample</th>
<th>Type of alloy</th>
<th>Calculated composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Nd$<em>2$Fe$</em>{14}$B + 5 wt.% Fe</td>
<td>Nd$<em>{11}$Fe$</em>{83}$B$_6$</td>
</tr>
<tr>
<td>A2</td>
<td>Nd$<em>2$Fe$</em>{14}$B + 10 wt.% Fe</td>
<td>Nd$<em>{10.5}$Fe$</em>{84}$B$_5.5$</td>
</tr>
<tr>
<td>A3</td>
<td>Nd$<em>2$Fe$</em>{14}$B + 15 wt.% Fe</td>
<td>Nd$<em>{10}$Fe$</em>{85}$B$_5$</td>
</tr>
<tr>
<td>A4</td>
<td>Nd$<em>2$Fe$</em>{14}$B + 20 wt.% Fe</td>
<td>Nd$<em>{9.3}$Fe$</em>{85.8}$B$_4.9$</td>
</tr>
<tr>
<td>A5</td>
<td>Nd$<em>2$Fe$</em>{14}$B + 25 wt.% Fe</td>
<td>Nd$<em>{8.5}$Fe$</em>{87.2}$B$_{3.3}$</td>
</tr>
<tr>
<td>A6</td>
<td>Nd$<em>2$Fe$</em>{14}$B + 30 wt.% Fe</td>
<td>Nd$<em>{7.9}$Fe$</em>{88.1}$B$_{4}$</td>
</tr>
<tr>
<td>A7</td>
<td>Nd$<em>2$Fe$</em>{14}$B + 35 wt.% Fe</td>
<td>Nd$<em>{7.3}$Fe$</em>{89.1}$B$_{3.6}$</td>
</tr>
</tbody>
</table>

The alloys were melt spun with 30 m/s linear speed of the copper wheel, in order to obtain amorphous or near-amorphous alloys. The samples were annealed in vacuum between 650°C and 750°C for 3 to 5 minutes.

3. RESULTS AND DISCUSSIONS

Table 2 reproduces the results after the treatments described above for some magnetic properties: saturation magnetization $M_S$, remanence $M_r$, intrinsic coercivity, $H_c$, and remanence ratio $M_r/M_S$. It can be seen, that for the most treatments and alloys, $M_r/M_S > 0.5$. That means that the magnets are “spring magnets”, hardened by exchange interactions.

Table 2

Magnetic properties of melt spun NdFeB alloy ribbon after different annealing treatments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing conditions</th>
<th>Magnetic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Temperature °C</td>
<td>Time [min]</td>
</tr>
<tr>
<td>A1.1</td>
<td>650</td>
<td>5</td>
</tr>
<tr>
<td>A1.2</td>
<td>750</td>
<td>5</td>
</tr>
<tr>
<td>A2.1</td>
<td>650</td>
<td>3</td>
</tr>
<tr>
<td>A2.2</td>
<td>750</td>
<td>3</td>
</tr>
<tr>
<td>A3.1</td>
<td>650</td>
<td>5</td>
</tr>
<tr>
<td>A3.2</td>
<td>750</td>
<td>3</td>
</tr>
<tr>
<td>A4.1</td>
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<td>5</td>
</tr>
<tr>
<td>A4.2</td>
<td>750</td>
<td>3</td>
</tr>
<tr>
<td>A5.1</td>
<td>695</td>
<td>5</td>
</tr>
<tr>
<td>A5.2</td>
<td>726</td>
<td>5</td>
</tr>
</tbody>
</table>
In Fig. 1 we plotted $\Delta H_c$ as a function of the $\alpha$-Fe content in the Nd$_2$Fe$_{14}$B/$\alpha$-Fe composites. The reduction of the intrinsic coercive force between 5 wt.% $\alpha$-Fe and 35 wt.% $\alpha$-Fe additions is consistent with that reported by Zern et al. [6].

Fig. 1. – Intrinsic coercivity of Nd$_2$Fe$_{14}$B/$\alpha$-Fe nanocomposites with exchange hardening, in dependence with the $\alpha$-Fe content.

We try to find an explanation of such a behaviour. For this, we must remark, in connection with the above mentioned facts, that in nanocomposites with exchange hardening, if the grain size of the soft magnetic phase, supposed to be here, for simplicity, a sphere, is larger than twice the critical length (exchange length, which is around the width of a domain wall) that means for
Nd$_2$Fe$_{14}$B/α-Fe around 100 Å, we will have an inner decoupled spherical region of radius $R$ in the middle of the grain (Fig. 2).

![Fig. 2. – A soft spherical inclusion, inside a hard phase of magnetization $M_r$ and magnetic field $H_d$.](image)

We suppose that the nanocomposite permanent magnetic material, in which is imbedded our soft Fe sphere $R$, is like an ideal magnet (with a rigid magnetisation) having in the working point the remanent magnetisation $M_r$. The working point is characterized by a demagnetization field $H_d$, oriented against the magnetization. We suppose also, that $M_r$ and $H_d$ are uniform.

In this hypothesis, we can write, for the regions 1 (soft) and 2 (hard) for the scalar potential $V$, the Laplace equation

$$\Delta V = 0. \quad (3)$$

In spherical coordinates (symmetry after the azimuthal angle $\phi$) equation (3) can be rewritten:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial V}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial V}{\partial \theta} \right) = 0,$$

with solutions in our two regions 1 and 2

$$V_1 = ar \cos \theta$$

$$V_2 = -H_d \cos \theta + \frac{b}{r^2} \cos \theta,$$

where $a$ and $b$ must be determined from the boundary conditions for the tangential field and for the normal component of the induction:

$$H_{t1} = H_{t2} \quad \text{at} \quad r = R,$$

$$B_{n1} = B_{n2} \quad \text{at} \quad r = R. \quad (5)$$

The boundary conditions (5) are equivalent with
\[ -\frac{1}{r} \frac{\partial V_1}{\partial \theta} = -\frac{1}{r} \frac{\partial V_2}{\partial \theta} \quad \text{for} \quad r = R \]
\[ -\mu_m \frac{\partial V_1}{\partial r} = -\frac{\partial V_2}{\partial r} + M_r \cos \theta, \quad \text{for} \quad r = R, \quad (6) \]

where $\mu_m$ is the relative permeability of the soft region against the hard magnet (we assume that region 2 is an ideal hard magnetic material, with the relative permeability equal with the unity).

The boundary conditions (6) determine the values of the coefficients $a$ and $b$ and the magnetic potentials become

\[ V_1 = \frac{3H_d + M_r}{\mu_m + 2} - r \cos \theta, \quad (7) \]
\[ V_2 = -H_d r \cos \theta + \left( \frac{\mu_m - 1}{\mu_m + 2} - \frac{M_r}{\mu_m + 2} \right) \frac{R^3}{r^2} \cos \theta. \]

Because $r \cdot \cos \theta = z$, we can calculate the magnetic field and the corresponding induction in the soft phase, as:

\[ H_{1z} = -\frac{\partial V}{\partial Z} = \frac{3H_d + M_r}{\mu_m + 2}, \]
\[ B_{1z} = \mu_0 \mu_m H_{1z} = \mu_0 \frac{\mu_m}{\mu_m + 2} (3H_d + M_r), \quad (8) \]

which are uniform in our approximation.

Taking into account that the demagnetizing field is $H_d = -N M_r$, where $N$ is the demagnetizing factor the relation (8) become

\[ H_{1z} = \frac{1 - 3N}{\mu_m + 2} M_r, \quad (8') \]
\[ B_{1z} = \mu_0 \frac{\mu_m}{\mu_m + 2} (1 - 3N) M_r. \]

It is obvious from (8'), that if $N > \frac{1}{3}$, than $B_{1z} < 0$, what means, that it is oriented antiparallel to the magnetisation of the hard magnetic phase.

If we consider the demagnetization curve in Fig. 3, of an ideal magnet, than we can write:

\[ B = \frac{\mu_0 H}{\tan \alpha} = \mu_0 H + \mu_0 M_r = (1 - N) \mu_0 M_r \]

and from here:
For our ideal magnet, the \((BH)_{\text{max}}\) point will have \(\alpha = 45^\circ\) with \(N = 1/2\) (from (9)) and \(B_{12} < 0\); in this situation the soft inclusion is a nucleation region for reversed domain magnetization. Such permanent magnets with soft iron inclusions (respectively decoupled soft regions) can work only in demagnetizing fields corresponding to a demagnetizing factor of \(N < 1/3\). That means that the soft phase must have a shape similar to the geometry of an elongated ellipsoid.

The magnetization of the soft region can be deduced from relations (8')

\[
M_I = \frac{\mu_m - \frac{3}{2}(1-3N)M_r}{\mu_m + 2} \leq M_r,
\]

in other words, the soft iron inclusions or the decoupled soft Fe regions cannot contribute to the enhancement of the induction. This is possible only for the coupled Fe regions in nanocomposites, for which we will have a remanence ratio \(M_I/M_S > 0.5\), which will mean, that the exchange hardened nanocomposite becomes anisotropic after the magnetizing direction of the isotropic nanocomposite.

If the content of the \(\alpha\)-Fe phase increase, than technologically, the dimensions and the geometry of the Fe grains cannot be controlled and maintained in narrow limits, the effect being the sharp decrease of the magnetic performances (reduced remanence and intrinsic coercivity).

The only one positive effect of the small soft inclusions (in nanocomposites and in “classical” permanent magnets) is the smaller price of the raw materials needed to manufacture a given volume of the permanent magnet.
We are looking now, if we can find, in the hypothesis of the Fe grains with only positive contributions, after a maximum number of that $\alpha$-Fe grains. The maximum number of such soft Fe inclusions is done by the condition that the magnetostatic energy of our chosen moment $\vec{m}_1$ must be still smaller than all dipolar magnetostatic interactions of the moment with the surrounding neighbors:

$$\frac{1}{2} \mu_0 \vec{m}_1 \vec{H}_1 \leq -\frac{\mu_0}{4\pi} \sum_i \left( \frac{3(\vec{m}_i \vec{r}_i) \vec{r}_i}{r_i^5} - \frac{\vec{m}_i}{r_i^3} \right) \vec{m}_1,$$

(10)

where the summation is extended over all neighbors with the moment $\vec{m}_i$ and the position vectors $\vec{r}_i$.

If we suppose that all $\vec{m}_i$ are parallel and the distribution of $\vec{m}_i$ is symmetrically around $\vec{m}_1$, than the right hand member of (8) is always equal zero and the condition is fulfilled. In reality, such symmetric geometry’s are impossible to be built and so we must take in the account nonuniform magnetization across the volume of the magnetic inclusions, having also not spherical shapes.

4. CONCLUSIONS

Our analysis showed that the existence in Nd$_2$Fe$_{14}$B/$\alpha$-Fe nanocomposites of soft $\alpha$-Fe inclusions in the Nd$_2$Fe$_{14}$B grains, with dimensions beyond the critical diameter (around 10–20 nm) causes a strong reduction of the coercivity and cannot contribute to the magnetisation enhancement of the nanocomposite.

The reduction of the coercivity of Nd$_2$Fe$_{14}$B/$\alpha$-Fe composites between 5 wt.% and 35 wt.% Fe excess is of 4–5 times, in accordance with previously reported values. The reduction of the coercivity when the $\alpha$-Fe content increases in Nd$_2$Fe$_{14}$B/$\alpha$-Fe nanocomposites, hardened through exchange interactions, is continuous; the reduction of the coercivity is probably done by decoupled Fe regions, always present in large sized Fe grains; it is not possible to establish an upper limit of the Fe content.

In sintered NdFeB permanent magnets, it is possible to have soft $\alpha$-Fe inclusions in the Nd$_2$Fe$_{14}$B grains, but such permanent magnets can be used only in demagnetizing fields smaller than $N \cdot M_r$, where $N$ is the demagnetizing factor, which must be $N < 1/3$ (assuming a spherical shape for the inclusions). The $\alpha$-Fe inclusions in the hard Nd$_2$Fe$_{14}$B grains cause a reduction not only of the coercivity, but also of the magnetisation of the permanent magnets.
REFERENCES