Production and Characterization of Nanostructured Powders of Nd$_2$Fe$_{14}$B and Fe$_{90}$Al$_{10}$ by Mechanical Alloying

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Abstract: The objective of this work is to evaluate the applicability of exchange coupling between nanoparticles of Nd$_2$Fe$_{14}$B (hard magnetic material) and Fe$_{90}$Al$_{10}$ (soft magnetic material), as permanent magnets produced by surfactant-assisted mechanical alloying. The obtained powders were then mixed with 85% of the Nd$_2$Fe$_{14}$B system and 15% of the Fe$_{90}$Al$_{10}$ system and subsequently sintered at 300 °C, 400 °C and 500 °C for one hour. The results obtained by Mössbauer spectrometry (MS) show a ferromagnetic behavior with six magnetic sites represented by sextets (16k1, 16k2, 8j1, 8j2, 4c and 4e), characteristic of the Nd$_2$Fe$_{14}$B system. X-ray diffraction (XRD) results show a tetragonal and BCC structure for the Nd$_2$Fe$_{14}$B and FeAl systems, respectively. The results obtained by vibrating sample magnetometry (VSM), for mixtures of the Nd$_2$Fe$_{14}$B and Fe$_{90}$Al$_{10}$ systems sintered at 300 °C, 400 °C and 500 °C, allow for the conclusion that the coercive field (Hc) decreases drastically with temperature and the percentage of soft phase at values of Hc = 132 Oe compared to the coercive field values reported for Nd$_2$Fe$_{14}$B Hc = 6883 Oe, respectively. Images obtained by transmission electron microscopy (TEM), for the Fe$_{90}$Al$_{10}$ system, show a tendency for the nanoparticles to agglomerate.

Keywords: magnetic materials; Mössbauer spectrometry; mechanical alloying; nanoparticle

1. Introduction

Permanent magnets based on rare earth (RE) elements, such as Nd$_2$Fe$_{14}$B, play a fundamental role in current and emerging technologies; they are found in commonly used devices (computers, speakers, smartphones, etc.), in the development of electric vehicles, and are an indispensable input for the construction of electrical generators capable of producing electrical energy from renewable natural sources such as water (hydroelectric power), wind (wind power) and the sea (wave energy) [1–7]. For this reason, the design of high-performance permanent magnets represents a need at the industrial level [1,2,5–7]. Permanent magnets usually contain large amounts of RE and other elements that are difficult to supply, such as Pr, Sm, Dy, Tb, Nd and Co, most of which are mined in foreign countries such as China, Congo, Russia and the United States [1–4]. Therefore, a huge gap crisis has been generated between the supply and demand of these magnets due to the unavailability of these raw materials and the difficulty in supplying them [1–3]. Taking into account this problem, recent studies have focused on the search for alternatives to produce magnets with a high energy density (BH)max using the smallest possible amount of rare earths [1,2,5,7–10]. Thus, the development of producing a two-phase nanocomposite formed by two magnetic phases, a hard one with high anisotropy (NdFeB or SmCo) coupled with a soft one with high magnetization (Fe, FeSi or FeCo), has gained great relevance in recent years and is considered the new generation of permanent magnets [1,4,7–11]. These exchange-coupled magnets average the magnetization and anisotropy of the two
constituents [8]. However, to have a positive impact on (BH)max, one of the direct effects is the improvement of the coercivity by the reduction of the grain size, which should be proportional to the width of the hard phase domain wall, allowing for the optimization of the exchange coupling [1–4,8]. The great challenge for researchers today remains in designing nanocomposites at a nanometer scale where the separation between hard and soft grains does not exceed 50 nm [1–4,8]. Recently, it has been shown that one process route to obtain nanoparticles with grain sizes smaller than 30 nm is by surfactant-assisted mechanical alloying [12]. In this work, Nd$_2$Fe$_{14}$B and Fe$_{90}$Al$_{10}$ samples produced by arc melting and surfactant-assisted mechanical alloying were structurally and magnetically characterized. In addition, the exchange coupling study of a nanocomposite formed by Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ and heat treated at different temperatures (300 °C, 400 °C and 500 °C) for one hour was carried out.

2. Results
2.1. Fe$_{90}$Al$_{10}$ System

Figure 1 shows the X-ray diffraction patterns of the Fe$_{90}$Al$_{10}$ arc furnace melt powders, sintered at 1000 °C for 7 days, and subsequently mechanically alloyed with oleic acid as a surfactant for 24 and 48 h. Here, we can observe that for the three diffractograms, there is only the presence of the phase corresponding to the Fe$_{90}$Al$_{10}$ system, with a BCC (cubic) structure and lattice parameter of (2.88 Å) [13–15]. This is a consequence of the effect of the milling time by not promoting secondary phases. Additionally, as shown in Table 1, we can observe the X-ray parameters (lattice parameter, crystallite size and weight fraction) of the crystalline phases present in the diffractograms of Figure 1, which were refined with an FeAl phase.

Figure 2 shows the TEM images of the Fe$_{90}$Al$_{10}$ nanoparticles obtained by surfactant-assisted mechanical alloying after 48 h. It can be observed that the milling time reduces the particle size with an irregular shape with an average width in the range of 30–70 nm and a length of 80–250 nm after 48 h of milling time, promoting agglomeration [12].

![Figure 1. XRD of the Fe$_{90}$Al$_{10}$ system with thermal treatment (TT) at 1000 °C for 7 days and mechanically alloyed with oleic acid as a surfactant for 24 and 48 h, respectively.](image-url)
Table 1. XRD parameters of the Fe$_{90}$Al$_{10}$ system with thermal treatment at 1000 °C for 7 days and mechanically alloyed with oleic acid as a surfactant for 24 and 48 h of milling time, respectively (the (a) column corresponds to the lattice parameters; the columns with (Φ$_{\text{per}}$) correspond to the mean crystallite size perpendicular to the radiation, the column with (Φ$_{\text{par}}$) corresponds to the mean crystallite size parallel to the radiation).

| Time  | Density (g/cm$^3$) ± 0.04 | Volume (Å$^3$) ± 0.04 | a (Å) ± 0.04 | Φ$_{\text{per}}$ (nm) ± 0.5 | Φ$_{\text{par}}$ (nm) ± 0.5 |
|-------|--------------------------|------------------------|--------------|---------------------------|---------------------------|
| 0 h   | 6.96 ± 0.04              | 24.041 ± 0.04          | 2.88 ± 0.04  | 28.8 ± 0.5                | 14.4 ± 0.5                |
| 24 h  | 6.99 ± 0.04              | 23.937 ± 0.04          | 2.88 ± 0.04  | 21.7 ± 0.5                | 18.1 ± 0.5                |
| 48 h  | 6.97 ± 0.04              | 23.990 ± 0.04          | 2.88 ± 0.04  | 24.8 ± 0.5                | 12.4 ± 0.5                |

Figure 1. XRD of the Fe$_{90}$Al$_{10}$ system with thermal treatment (TT) at 1000 °C for 7 days and mechanically alloyed with oleic acid as a surfactant for 24 and 48 h, respectively.

Figure 2. Transmission electron microscopy (TEM) images of the Fe$_{90}$Al$_{10}$ nanoparticles obtained by surfactant-assisted mechanical alloying after 48 h. It can be observed that the milling time reduces the particle size with an irregular shape with an average width in the range of 30–70 nm and a length of 80–250 nm after 48 h of milling time, promoting agglomeration [12].

Figure 3 shows the Mössbauer spectra and the hyperfine field probability distributions of the arc furnace powders of the Fe$_{90}$Al$_{10}$ system, sintered at 1000 °C for 7 days. The Mössbauer spectra were fitted with one component (sextet) associated with the Fe$_{90}$Al$_{10}$ system, indicating a ferromagnetic behavior which presents a disorderly character given by the half-width of the line due to the reduction of the particle size by the milling process [13,15]. This is a consequence of the high content of Fe in the sample and the thermal treatment carried out on it at 1000 °C followed by quenching in ice water, and this treatment retains the high-temperature disordered structure. Due to the line width, the spectra of the sample was fitted with a magnetic hyperfine field distribution (HMFD). The result of the HMFD is shown on the right side of Figure 3, where it is observed that the distribution has a single site, or more likely a site near 310 kOe. After fitting, a mean hyperfine field of 318 kOe is obtained which is smaller than the field of pure Fe as a consequence of the substitution of Fe by Al atoms. These results are similar to those reported by other authors [13].

Figure 4 shows the spectra of the sample mechanically alloyed with oleic acid as a surfactant for 48 h of milling time, which was fitted with an HMFD (blue line), whose spectral area corresponds to 70%, with a mean-field of 320 kOe, and a doublet whose spectral area is 30% (red line) [13]. This behavior can be explained because the mechanical alloying promotes the diffusion of atoms in the BCC structure. Therefore, now 70% of the Fe sites will be surrounded by many first neighbors of Fe, leading to ferromagnetic behavior, and 30% of the remaining Fe sites will be surrounded by first neighbors of Al, leading to paramagnetic behavior. This interpretation is due to the unique presence of the
BCC phase, as given by XRD. Here, the average hyperfine field of the milled sample is higher than the average hyperfine field of the thermally treated sample, indicating that the ferromagnetic sites of the milled sample are richer in Fe than the sites of the thermally treated sample (fewer atoms of the first neighbors). Mössbauer parameters are shown in Table 2.

Figure 3. Mössbauer spectra and its corresponding probability distribution of the Fe$_{90}$Al$_{10}$ system with thermal treatment (TT) at 1000 °C for 7 days.

Figure 4. Mössbauer spectra of the Fe$_{90}$Al$_{10}$ system with thermal treatment at 1000 °C for 7 days and milled for 48 h with oleic acid as a surfactant. The fit of the spectrum is given by the theoretical line (purple line), the HMFD (blue line) and the doublet (red line).

Table 2. Mössbauer parameters and probability distribution of the Fe$_{90}$Al$_{10}$ system with thermal treatment at 1000 °C for 7 days and 48 h of milling with oleic acid as a surfactant (the column with (δ) corresponds to the isomer shift values; the column with (Γ) corresponds to the line widths; the column with (Qs) corresponds to the quadrupole splitting; the column with (HF) corresponds to the hyperfine field; and the line with (HMDF) corresponds to the magnetic hyperfine field distribution).

| Time  | Component | δ (mm/s) ±0.005 | Γ (mm/s) ±0.005 | Qs (mm/s) ±0.005 | HF (kOe) ±0.4 | Spectral Area % |
|-------|-----------|-----------------|-----------------|------------------|-------------|----------------|
| 0 h   | HMDF      | 0.033           | 0.026           | 318.2            |             | 62.5           |
| 48 h  | HMDF      | 0.038           | 0.323           | 200.1            | 888         | 37.5           |

Figure 5 shows the hysteresis loop of the Fe$_{90}$Al$_{10}$ system and Table 3 shows the values of the extrinsic magnetic properties of the material: saturation magnetization (Ms), remanent magnetization (Mr), and coercive field (Hc).
remanent magnetization (Mr) and coercive field (Hc) obtained from the hysteresis loops. These results indicate that the samples have ferromagnetic behavior (soft magnetic material), according to the results of the Mössbauer spectra. Additionally, it can be seen that all magnetic properties decrease as the milling time increases. This is due to the reduction in particle size, which causes the diffusion of Fe atoms and promotes paramagnetic sites in the system, as observed in Mössbauer, possibly due to the appearance of paramagnetic sites, as Mössbauer showed.

Figure 5. Hysteresis loops Fe$_{90}$Al$_{10}$ system with thermal treatment at 1000 °C for 7 days and mechanically alloyed for 24 and 48 h, respectively.

Table 3. Extrinsic magnetic properties of the Fe$_{90}$Al$_{10}$ system with thermal treatment at 1000 °C for 7 days and milled for 24 and 48 h with oleic acid as a surfactant (the column with (Hc) corresponds to the coercive field; the column with (Mr) corresponds to the remanent magnetization; and the column with (Ms) corresponds to the saturation magnetization).

| Milling Time | Hc (Oe) ±0.4 | Mr (emu/g) ±0.4 | Ms (emu/g) ±0.4 |
|-------------|--------------|----------------|-----------------|
| 0 h         | 67.5         | 6.8            | 225.2           |
| 24 h        | 33.3         | 2.3            | 173.7           |
| 48 h        | 26.6         | 1.7            | 137.9           |
2.2. Nd$_2$Fe$_{14}$B System

Figure 6 shows the X-ray diffraction patterns of the commercial powder of the Nd$_2$Fe$_{14}$B system and the powder produced by mechanical alloying assisted with oleic acid as a surfactant for 24 and 48 h of milling time. The structural parameters (lattice parameter, crystallite size and fraction of volume) of the crystalline phases present in the diffractograms of Figure 6 are shown in Table 4. Here, we can observe that before and after milling time, the powders have a tetragonal structure associated with the Nd$_2$Fe$_{14}$B phase (hard phase) [1,4]. However, with the increase in the milling time, we can observe an increase in the intensity of the peak occupied by the position (2θ = 26.5°, this peak was not possible to associate with any known phase). Furthermore, it is observed that the intensity of the peaks of the hard phase decreases and the half-width of the line increases, indicating a reduction of the crystallite size. The XRD parameters obtained after the Rietveld refinement indicate that the perpendicular and parallel crystallite sizes, and also the lattice parameters, decrease with the milling time. This result indicates that the milling process is effective in reducing the size of crystallites and increasing micro-tensions, which explains why the half-width of the line of the diffractogram increases. In addition, surfactant-assisted mechanical alloying promotes particle size reduction.

![Figure 6. XRD of the Nd$_2$Fe$_{14}$B system without milling and mechanically milled with oleic acid as a surfactant for 24 and 48 h, respectively.](image)

Table 4. Structural parameters of the original system Nd$_2$Fe$_{14}$B and mechanically alloyed with oleic acid as a surfactant for 24 and 48 h, respectively (the columns (a and c) correspond to the lattice parameters).

| Milling Time | Density (g/cm$^3$) | Volume (Å$^3$) | a (Å) | c (Å) | Φ$_{per}$ (nm) | Φ$_{par}$ (nm) |
|--------------|--------------------|----------------|-------|-------|----------------|----------------|
| 0 h          | 7.58 ± 0.04        | 947.26 ± 0.04  | 8.80  | 12.20 | 54.7           | 34.4           |
| 24 h         | 8.25 ± 0.04        | 931.63 ± 0.04  | 8.75  | 12.14 | 8.0            | 15.2           |
| 48 h         | 9.09 ± 0.04        | 899.08 ± 0.04  | 8.63  | 12.04 | 14.8           | 22.0           |

The Mössbauer spectrum of the powders of the Nd$_2$Fe$_{14}$B system mechanically alloyed with oleic acid as a surfactant for 48 h of milling time is shown in Figure 7. The Mössbauer
parameters of the sample are presented in Table 5. The sample was fitted with six magnetic sites (sextets) associated with six non-equivalent crystallographic iron sites corresponding to the hard magnetic phase Nd$_2$Fe$_{14}$B (16K$_1$, 16K$_2$, 8j$_1$, 8j$_2$, 4c, and 4e); which indicates that the sample presents a ferromagnetic behavior [16,17].

Table 5. Mössbauer parameters of the commercial Nd$_2$Fe$_{14}$B system for 48 h of milling time with oleic acid as a surfactant. The column with (HF) corresponds to the hyperfine field; and the lines with (J1, J2, K1, K2, C, E) correspond to the non-equivalent crystallographic iron site for Nd$_2$Fe$_{14}$B.

| Milling Time | Component | $\delta$ (mm/s) ±0.005 | $\Gamma$ (mm/s) ±0.005 | $Q_s$ (mm/s) ±0.005 | HF (kOe) ±0.4 | Spectral Area (%) |
|--------------|-----------|------------------------|------------------------|---------------------|---------------|------------------|
| 48 h         | J1        | -0.074                 | 0.165                  | 0.171               | 282.3         | 17.4             |
|              | J2        | -0.017                 | 0.231                  | 0.112               | 329.1         | 19.6             |
|              | K1        | -0.054                 | 0.174                  | 0.097               | 267.1         | 10.8             |
|              | K2        | 0.026                  | 0.234                  | 0.263               | 346.4         | 17.0             |
|              | C         | -0.006                 | 0.239                  | 0.114               | 249.2         | 10.5             |
|              | E         | -0.097                 | 0.181                  | 0.114               | 300.4         | 24.5             |

Figure 8 shows the hysteresis loops of the commercial powder of the Nd$_2$Fe$_{14}$B system and the powder obtained by the milling process with surfactant for 24 and 48 h at room temperature. Table 6 shows the values of the extrinsic magnetic properties: saturation magnetization (Ms), remanent magnetization (Mr) and coercive field (Hc) obtained from the hysteresis loops. The result showed the characteristic behavior of a single-phase hard magnet with no kinks in the demagnetization curve, with coercive field values in the range of 2350.9 to 6883.4 Oe, saturation magnetization values in the range of 116 to 129 emu/g, and values of remanent magnetization values in the range of 48.4 to 84.5 emu/g. The highest coercivity of 6883.4 Oe was obtained in the pure sample. Coercivity values decrease with the decrease in particle size, which means that particles in the nanometric order will lead to lower coercivity, although the lowest coercivity range occurs at 24 h of milling time. The same decrease occurs for the remanent magnetization and saturation magnetization when the particle size decreases.
1.0, confirming the absence of the tetragonal phase of Nd$_2$Fe$_{14}$B presented in Table 8. The sample was fitted with a sextet and a singlet corresponding to perpendicular and parallel crystallite sizes increase for the Fe$_{90}$Al$_{10}$ system, while for the Nd$_2$Fe$_{14}$B phase they have an irregular behavior; however, the low intensity of this phase in the diffractogram can cause errors in the measurement of these values. The Mössbauer spectra of the Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ system sintered for one hour at 300 °C are shown in Figure 10. The Mössbauer parameters for each sample are presented in Table 7. Here, it is observed that for all temperatures that the BCC structure of the Fe$_{90}$Al$_{10}$ system [13] predominates and the tetragonal structure of the Nd$_2$Fe$_{14}$B system disappears almost completely. The parameters obtained by Rietveld refinement indicate that the majority phase is Fe$_{90}$Al$_{10}$ with a volume fraction of almost 1,0, confirming the absence of the tetragonal phase of Nd$_2$Fe$_{14}$B in the mixing samples. This is possibly due to the size of the crystallites of the Fe$_{90}$Al$_{10}$ system, and/or that the soft phase mass ratio is excessive, which makes it possible to identify only this phase. The perpendicular and parallel crystallite sizes increase for the Fe$_{90}$Al$_{10}$ system and show a significant reduction for the Nd$_2$Fe$_{14}$B system. The lattice parameters remain constant for the Fe$_{90}$Al$_{10}$ system, while for the Nd$_2$Fe$_{14}$B phase they have an irregular behavior; however, the low intensity of this phase in the diffractogram can cause errors in the measurement of these values. The Mössbauer spectra of the Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ system sintered for one hour at 300 °C are shown in Figure 10. The Mössbauer parameters for each sample are presented in Table 8. The sample was fitted with a sextet and a singlet corresponding to the Fe$_{90}$Al$_{10}$ phase [16]. The spectra corresponding to the tetragonal phase of Nd$_2$Fe$_{14}$B do not appear, which effectively shows the absence of this phase in the mixture samples as observed by XRD.

Table 6. Extrinsic magnetic properties of the Nd$_2$Fe$_{14}$B system and milled for 24 and 48 h with oleic acid as surfactant.

| Time   | Hc (Oe) ±0.4 | Mr (emu/g) ±0.4 | Ms (emu/g) ±0.4 |
|--------|--------------|----------------|----------------|
| 0 h    | 6883.4       | 84.5           | 118.4          |
| 24 h   | 1979.2       | 52.7           | 129.3          |
| 48 h   | 2350.9       | 48.3           | 115.9          |

2.3. Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ Nanocomposite System

Figure 9 shows the X-ray diffraction patterns of the Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ system thermally treated at 300 °C, 400 °C and 500 °C. The X-ray parameters (lattice parameter, crystallite size and volume fraction) of the crystalline phases present in the diffractograms of Figure 9 are shown in Table 7. Here, it is observed that for all temperatures that the BCC structure of the Fe$_{90}$Al$_{10}$ system [13] predominates and the tetragonal structure of the Nd$_2$Fe$_{14}$B system disappears almost completely. The parameters obtained by Rietveld refinement indicate that the majority phase is Fe$_{90}$Al$_{10}$ with a volume fraction of almost 1,0, confirming the absence of the tetragonal phase of Nd$_2$Fe$_{14}$B in the mixing samples. This is possibly due to the size of the crystallites of the Fe$_{90}$Al$_{10}$ system, and/or that the soft phase mass ratio is excessive, which makes it possible to identify only this phase. The perpendicular and parallel crystallite sizes increase for the Fe$_{90}$Al$_{10}$ system and show a significant reduction for the Nd$_2$Fe$_{14}$B system. The lattice parameters remain constant for the Fe$_{90}$Al$_{10}$ system, while for the Nd$_2$Fe$_{14}$B phase they have an irregular behavior; however, the low intensity of this phase in the diffractogram can cause errors in the measurement of these values. The Mössbauer spectra of the Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ system sintered for one hour at 300 °C are shown in Figure 10. The Mössbauer parameters for each sample are presented in Table 8. The sample was fitted with a sextet and a singlet corresponding to the Fe$_{90}$Al$_{10}$ phase [16]. The spectra corresponding to the tetragonal phase of Nd$_2$Fe$_{14}$B do not appear, which effectively shows the absence of this phase in the mixture samples as observed by XRD.

![Figure 8. Hysteresis loops of the Nd$_2$Fe$_{14}$B system and mechanically alloyed for 24 and 48 h, respectively.](image-url)
Figure 9. XRD of the sintered Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ systems at 300, 400 and 500 °C, respectively.

Table 7. XRD parameters of the sintered Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ system at 300, 400 and 500 °C, respectively.

| Temperature (°C) | Phase       | Density (g/cm$^3$) | Volume (Å$^3$) | a (Å)  | Φ$_{per}$ (nm) | Φ$_{par}$ (nm) |
|------------------|-------------|--------------------|----------------|--------|----------------|----------------|
| 300              | Fe$_{90}$Al$_{10}$ | 5.23 ± 0.04        | 23.39 ± 0.04   | 2.85 ± 0.04 | 47.2 ± 0.5     | 20.0 ± 0.5     |
| 400              | Fe$_{90}$Al$_{10}$ | 7.04 ± 0.04        | 29.75 ± 0.04   | 2.87 ± 0.04 | 62.6 ± 0.5     | 34.1 ± 0.5     |
| 500              | Fe$_{90}$Al$_{10}$ | 7.07 ± 0.04        | 23.67 ± 0.04   | 2.87 ± 0.04 | 43.9 ± 0.5     | 43.2 ± 0.5     |

Figure 10. Mössbauer spectra of the sintered Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ system for one hour at 300 °C.
Table 8. Mössbauer parameters of the sintered Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$ system for one hour at 300 °C.

| Component | $\delta$ (mm/s) $\pm 0.005$ | $\Gamma$ (mm/s) $\pm 0.005$ | $Qs$ (mm/s) $\pm 0.005$ | HF (kOe) $\pm 0.4$ | Spectral Area(%) |
|-----------|----------------|----------------|----------------|----------------|-----------------|
| Sextet    | 0.033          | 0.262          | -0.082         | 331.3          | 96              |
| Singlet   | -0.057         | 0.182          | 0.000          |                | 4               |

Figure 11 shows the hysteresis loops of the commercial powders of the Nd$_2$Fe$_{14}$B system and the powders obtained by mechanical alloying assisted with surfactant for 24 and 48 h of milling time at room temperature. Table 9 shows the values of the extrinsic magnetic properties: saturation magnetization (Ms), remanent magnetization (Mr) and coercive field (Hc) corresponding to the hysteresis loops. The hysteresis loops show a characteristic behavior of a single-phase soft magnet with no kinks in the demagnetization curve, with coercive field values in the range of 132 to 171 Oe, saturation magnetization values in the range of 138 to 173 emu/g, and remanent magnetization values in the range of 9 to 16 emu/g. The highest coercivity of 171 Oe was obtained in the sample sintered at 300 °C. As seen in Figure 11, the magnetic hardness offered by the tetragonal Nd$_2$Fe$_{14}$B phase is completely lost. Additionally, the increase in the sintering temperature decreases the magnetic properties, such as saturation magnetization (Ms), remanent magnetization (Mr) and coercive field (Hc).

Table 9. Extrinsic magnetic properties of the Nd$_2$Fe$_{14}$B system. Fe$_{90}$Al$_{10}$ sintered at 300, 400 and 500 °C, respectively.

| Temperature (°C) | Hc (Oe) ±0.4 | Mr (emu/g) ±0.4 | Ms (emu/g) ±0.4 |
|------------------|-------------|----------------|---------------|
| 300              | 171.2       | 16.5           | 173.2         |
| 400              | 149.1       | 12.0           | 162.9         |
| 500              | 132.2       | 9.9            | 138.6         |

3. Experimental Process

Fine Fe and Al powders of 99.5% and 99% purity were melted in an arc furnace and sintered at 1000 °C for seven (7) days. From the alloy obtained, powders were obtained with...
a diamond file. These powders and the fine powder of Nd$_2$Fe$_{14}$B (with a purity of 99% and an average particle size of 150) were mechanically alloyed with surfactant (oleic acid) in a planetary ball mill (Fritsch Pulverisette 5) at 280 rpm with a ball-to-powder ratio of 20/1 for 24 and 48 h milling times [18]. Finally, the soft (Fe$_{90}$Al$_{10}$) and hard (Nd$_2$Fe$_{14}$B) phases were mixed for 48 h, with milling times at 15% and 85%, respectively. Then, the mixture was heat treated at 300 °C, 400 °C and 500 °C for one hour. Structural and magnetic characterization were performed by X-ray diffraction (XRD), transmission electron microscopy (TEM), Mössbauer spectrometry (MS) and vibrating sample magnetometry (VSM). XRD measurements were performed at room temperature using Cu-Kα radiation. The diffraction patterns were refined using the Rietveld method using the GSAS program [19], from the refinement of the calibration sample (LaB$_6$). The images obtained by TEM show the morphology and size of the Nd$_2$Fe$_{14}$B nanoparticles. The Mössbauer spectra were fitted using Mosfit software [20], and were performed at room temperature using a $^{57}$Co (Rh) source with transmission geometry. The VSM measurements were obtained at room temperature, with an applied field up to 3 T, using a physical properties measurement system (PPMS) without taking demagnetization effects into consideration.

4. Conclusions

The Fe$_{90}$Al$_{10}$ alloy produced by surfactant-assisted mechanical alloying forms a soft magnetic material with a BCC structure. The milling process decreases the particle size to the nanometer scale, promoting a tendency to agglomeration [21]. The Mössbauer results showed that the hyperfine field of the material decreases with milling time, showing a paramagnetic site due to the substitution of aluminum atoms by iron atoms in its crystal structure. The commercial Nd$_2$Fe$_{14}$B alloy presents a tetragonal structure; this was mechanically alloyed, and assisted with surfactant in order to reduce the particle size. The Mössbauer results showed the presence of six magnetic sites (sextets), characteristic of the Nd$_2$Fe$_{14}$B unit cell [1–5]. The VSM results show a reduction of the coercive field with milling time, which is related to the increase of the amorphous part in the sample as a consequence of the milling time. The nanocomposite formed by (Nd$_2$Fe$_{14}$B/Fe$_{90}$Al$_{10}$), and heat treated at 300, 400 and 500 °C, does not show an exchange coupling between the two magnetic systems, evidencing a soft magnetic behavior, characteristic of the Fe$_{90}$Al$_{10}$ alloy, as observed by XRD.

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