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STUDY OF THE STRUCTURAL AND MAGNETIC PROPERTIES OF $GD_{0.257-X}ND_XFE_{0.743}$ AS OBTAINED BY MECHANICAL ALLOYING

Hugo Martínez Sánchez[1]
Yebrayl Rojas Martínez[2]
Dagoberto Oyola Lozano[2]
Humberto Bustos Rodríguez[2]

ABSTRACT

This paper presents the study of structural and magnetic properties in the composition $Gd_{0.257-x}Nd_xFe_{0.743}$ where x = 0, 0.1285, 0.257 prepared by mechanical alloying in an argon atmosphere and with a milling time of 72 hours using a high energy planetary mill. The magnetic and structural characterization was performed by Mössbauer Spectroscopy (MS) and X-Ray diffraction (XRD), respectively. The three patterns show an intense peak corresponding to the α-Fe phase. Its intensity decreases as Gd is replaced by Nd showing the minimum intensity for x =0.257, and at the same time it shows a progressive increase in the peak's width. These effects are attributed to the rich presence of Gd and/or Nd atoms in the iron sites. Mössbauer spectra were adjusted with hyperfine field distributions, sextets and singlets using the Mosfit program. The spectra show that by substituting the Gd with Nd atoms, the magnetic order is affected in such a way that iron sites appear and show magnetic disorder.

KEYWORDS: Mechanical Alloying, Mössbauer Spectroscopy, Rare Earth Alloys and Transition Metals, X-Ray Diffraction, Structural and Magnetic Properties.

ESTUDIO DE LAS PROPIEDADES ESTRUCTURALES Y MAGNÉTICAS DE $GD_{0.257-X}ND_XFE_{0.743}$ OBTENIDO POR ALEAMIENTO MECÁNICO

RESUMEN

En este trabajo presentamos el estudio de las propiedades estructurales y magnéticas de la composición $Gd_{0.257-x}Nd_xFe_{0.743}$ con x=0, 0.1285, 0.257 preparada por Aleamiento mecánico en atmósfera de argón y con tiempo de molienda de 72 horas, usando un molino planetario de alta energía. La caracterización magnética y estructural se realizó por Es-

[1] Licenciado en Matemáticas. Estudiante de maestría en Ciencias Física. Universidad del Tolima. Ibagué, Colombia.

[2] Físico. Doctor en Física. Universidad del Tolima. Ibagué, Colombia.

Author's Mailing Address: Martínez Sánchez, H. (Hugo): Universidad del Tolima, Barrio Santa Helena Parte Alta | Código Postal Nro. 730006299. Ibagué - Tolima - Colombia. Email: hugo.sanchez.16@hotmail.com

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pectroscopia Mössbauer (MS) y Difracción de rayos X (XRD) respectivamente. Los tres difractógramas presentan un pico intenso, correspondientes a la fase α-Fe, cuya intensidad disminuye a medida que se sustituye el Gd por el Nd, mostrándose la mínima intensidad cuando x=0.257, y a su vez se observa un incremento progresivo en su ancho, estos efectos se atribuyen a la rica presencia de átomos de Gd y/o Nd en los lugares del hierro. Los espectros Mössbauer se ajustaron con distribuciones de campo hiperfino, sextetos y singletes usando el programa Mosfit. Los espectros muestran que al sustituir los átomos de Gd por los de Nd el orden magnético se afecta de tal manera que aparecen sitios de hierro que muestran desorden magnético.

PALABRAS CLAVES: Aleamiento mecánico, espectroscopia Mössbauer, aleaciones de tierras raras y metales de transición, difracción de rayos X, propiedades estructurales y magnéticas.

ESTUDO DAS PROPRIEDADES ESTRUTURAIS E MAGNÉTICAS DE $GD_{0.257-x}ND_xFE_{0.743}$ OBTIDO POR MOAGEM MECÂNICA

RESUMO

Este artigo apresenta o estudo das propriedades estruturais e magnéticas da composição $Gd_{0.257-x}Nd_xFe_{0.743}$ x = 0, 0.1285, 0.257 preparado por liga mecânica sob árgon e com um tempo de 72 horas de moagem, utilizando um moinho High Energy. A caracterização estrutural e magnética foi realizada por Espectroscopia Mössbauer (MS) e difracção de raios-X (XRD), respectivamente. Os três difractogramas apresentam um pico forte correspondendo à fase α-Fe, sua intensidade diminui na medida que o Gd é substituído por Nd, que mostra a intensidade mínima quando x = 0.257, e por sua vez, um aumento progressivo na largura, e esses efeitos são atribuídos aos átomos de Gd e/ou Nd que estão presentes nos lugares do ferro. Os espectros Mössbauer foram ajustados com distribuições de campo hiperfino, sextetos e singletos usando o programa Mosfit. Os espectros mostram que substituindo átomos de Nd por Gd a ordem magnética é afetada de modo que aparecem sítios que apresentaram desordem ferromagnético.

PALAVRAS-CHAVE: Moagem mecánica, espectroscopia Mössbauer, ligas de terras raras e de metal de transição, XRD, propriedades estruturais e magnéticas.

1. INTRODUCTION

Rare earth elements (REE) and transition metal (TM) alloys have been studied by researchers because 4f orbital of REEs and 3d orbita lof TMs are unpaired. This allows interactions between their spins and produces magnetism. The study of GdFe, NdFe and GdNdFe alloys is important to understand the ferro or antiferromagnetic coupling of an REE (Gd and Nd) with a TM (Fe), as well as the behavior of their magnetic and magneto-optical properties when replacing Nd with Gd. Some investigations (Sallica, et al., 2009) show that these compounds have high magnetic anisotropy, high coercivity, high saturation magnetization, high Curie temperature and great polar magneto-optical Kerr effect, which is of great interest for the manufacturing of information storage devices and magnetic control systems. Other studies such as those performed by Chaudari, Cuomo and Gambino (1973) showed that saturation magnetization at 300K varies in Gd-Co systems when the composition of the REE present in the system is changed—the Curie temperature

varies with the changes made as well—making them the systems that best show the influence of the rare earth element on variations of the magnetic moment of alloys with transition metals. Zhang, et al. (2004) studied the effect of the substitution of Nd for Gd on the magnetic properties of nanocomposite magnets of $Nd_2Fe_{14}B$-α-Fe and compared them with those obtained when Nd was replaced by Y and Sm. They found that the exchange interactions due to the decrease of magnetocrystalline anisotropy improve. Recent research (Arrabal, et al., 2012) has also shown that the use of Nd or Gd improves the anticorrosion properties of Mg-Al-Mn alloys by up to 43%.

Dancygier (1987) studied the TbxFe1-x system, reporting that the best coercivity is obtained when x = 0.257, making these materials useful for applications such as magnetic memory media. It is of special interest to know the influence of the composition and milling time on the structural and magnetic properties of the compound $Gd_{0.257-x}Nd_xFe_{0.743}$ when x=0, 0.1285, 0.257. Pawlik, et al. (2004) studied the effects of production method and composition on the structure and magnetic properties of the $Nd_{10+x}Fe_{90-x}$ ($x = 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5$ and 4) system; their results reveal the existence of the crystalline phases α-Fe and Fe_2Nd_{17} when $x \leq 1.5$, while when $x > 1.5$ the α-Fe phase was not found, and only a homogeneous region attributed to the Nd_2Fe_{17} phase was observed. Shand, et al. (2011) studied the correlation between the structure and ferromagnetic properties of the $Gd_{100-x}Fe_x$ system ($0 \leq x \leq 40$) and found that alloys with ($3.8 \leq x \leq 12.7$) reveal a network of hcp-Gd crystalline grains surrounded by a non-crystalline phase of $Gd1–x_{eff}Fex_{eff}$, where x_{eff} is the effective concentration of iron within the amorphous region, which manifests itself in an unusual dependence between Curie temperature and coercivity.

This paper reports the structural and magnetic properties of the $Gd_{0.257-x}Nd_xFe_{0.743}$ system when x=0, 0.1285, 0.257, as obtained by mechanical alloying (Suryanarayana, 1887) with 72 hours of milling, when Gd is replaced by Nd. The study was performed using MS and XRD.

2. MATERIALS AND METHODS

High purity Gd, Nd and Fe powders (99.9%) were mixed in compositions of $Gd_{0.257}Fe_{0.743}$, $Gd_{0.1285}Nd_{0.1285}Fe_{0.743}$ and $Nd_{0.257}Fe_{0.743}$, and were mechanically alloyed in a high energy FRITSCH PULVERISETTE 7 planetary mill with stainless steel milling bowls measuring 50 ml in volume and spheres of the same material 11 mm in diameter, in an Ar atmosphere with a milling time of 72 hours at a speed of 280 revolutions per minute and with a balls-powder weight ratio of 20:1.

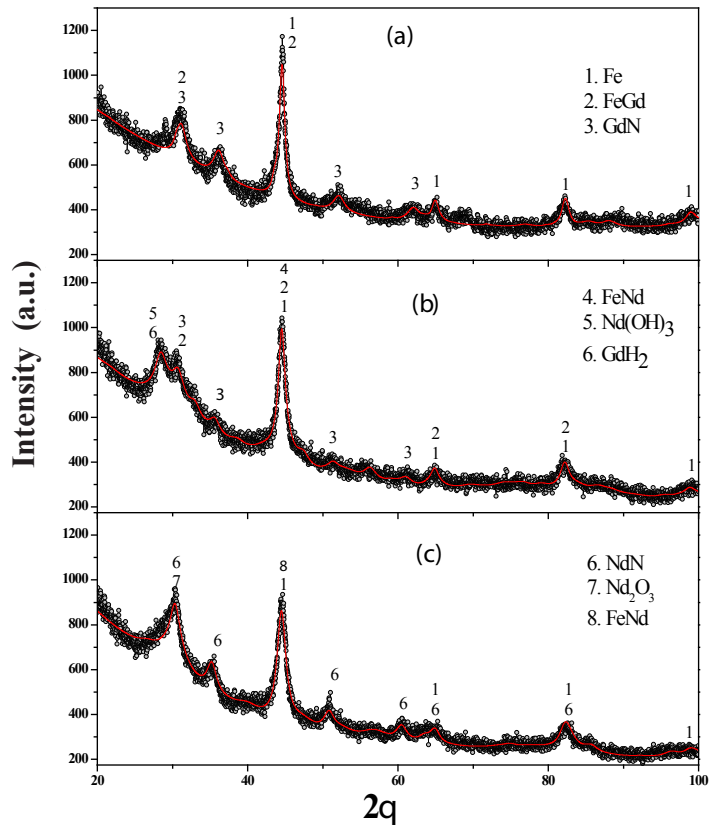
Mössbauer spectra were obtained at room temperature using a Mössbauer transmission spectrometer with a radioactive source of cobalt 57 immersed in a Rhodium (Rh) matrix and fitted with the MOSFIT program (Varret and Teillet). A standard sample of α-Fe was used as the calibration sample. X-ray analysis to establish the structure and size of the crystallite was performed at room temperature for all samples using a Cu k-alpha diffractometer, and the patterns obtained were adjusted using the MAUD program (Lutterotti et al., 1990).

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of mechanically alloyed powders in the compositions $Gd_{0.257}Fe_{0.743}$ (for x=0), $Gd_{0.1285}Nd_{0.1285}Fe_{0.743}$ (for x=0.1285) and $Nd_{0.257}Fe_{0.743}$ (for x=0.257), which were milled for 72 hours. Wide peaks of an α-Fe BCC phase can be observed in all the diffractograms.

The diffractogram for sample x = 0 exhibits the α-Fe phase with network parameter a = 2,866 Å in the peaks corresponding to the angles 2θ = 44.57 °, 64.96 °, 82.27 ° and 98.97 °. For different angles it presents the following phases: Fe5Gd with hexagonal structure and network parameters a = 4,634 Å and c = 4,145 Å and the GdN phase, which has a cubic structure with network parameter a = 4,944 Å.

Figure 1. X-ray diffraction patterns of samples (a) $Gd_{0.257}Fe_{0.743}$, (b) $Gd_{0.1285}Nd_{0.1285}Fe_{0.743}$ and (c) $Nd_{0.257}Fe_{0.743}$ with 72 hours of milling



The diffractogram for x=0.1285 exhibits the α-Fe phase with network parameter a=2,870 Å in the peaks corresponding to the angles 2θ=44.54 °, 64.88 ° and 82.19 °. For different angles it presents the following phases: Fe_5Gd, which has a hexagonal structure with network parameters a=4,746 Å and c=3,930 Å, the Fe_5Nd phase with a hexagonal structure and network parameters a=4,516 Å and c=4,401 Å, the GdN phase with a cubic structure and network parameter a = 5.138 Å, the GdH_2 phase with a cubic structure and network parameter a=5.432 Å and the $Nd(OH)_3$ phase with a hexagonal structure and network parameters a=5,882 Å and c=3,924 Å.

The diffractogram for x=0.257 exhibits the α-Fe phase with network parameter a=2,862 Å in the peaks corresponding to angles 2θ=44.50 °, 64.84 °, 82.35 ° and 99.03 °. For different angles it presents the following phases: Fe_5Nd with a hexagonal structure and network parameters a=4,741 Å and c=4,342 Å, the NdN phase having a cubic structure with network parameter a=5,061 Å, and finally the Nd_2O_3 phase, which has a hexagonal structure with network parameters a=3,825 Å and c=6.150 Å. The presence of the $Nd(OH)_3$, GdN, GdH_2, NdN and Nd_2O_3 subnetworks is attributed to contamination of the argon atmosphere during the preparation and milling process of the samples.Research conducted by Biondo, et al. (1997), Alonso, et al. (1992), and Spedding, et al. (1971) shows that the lanthanides react strongly with O, N and H. **Table 1** shows the X-ray parameters (phases, network parameters, crystallite size and volume fraction) of the three diffractograms.

TABLE 1. XRD PARAMETERS FOR COMPOSITIONS $GD_{0.257}FE_{0.743}$, $GD_{0.1285}ND_{0.1285}FE_{0.743}$ AND $ND_{0.257}FE_{0.743}$, MILLED FOR 72 HOURS

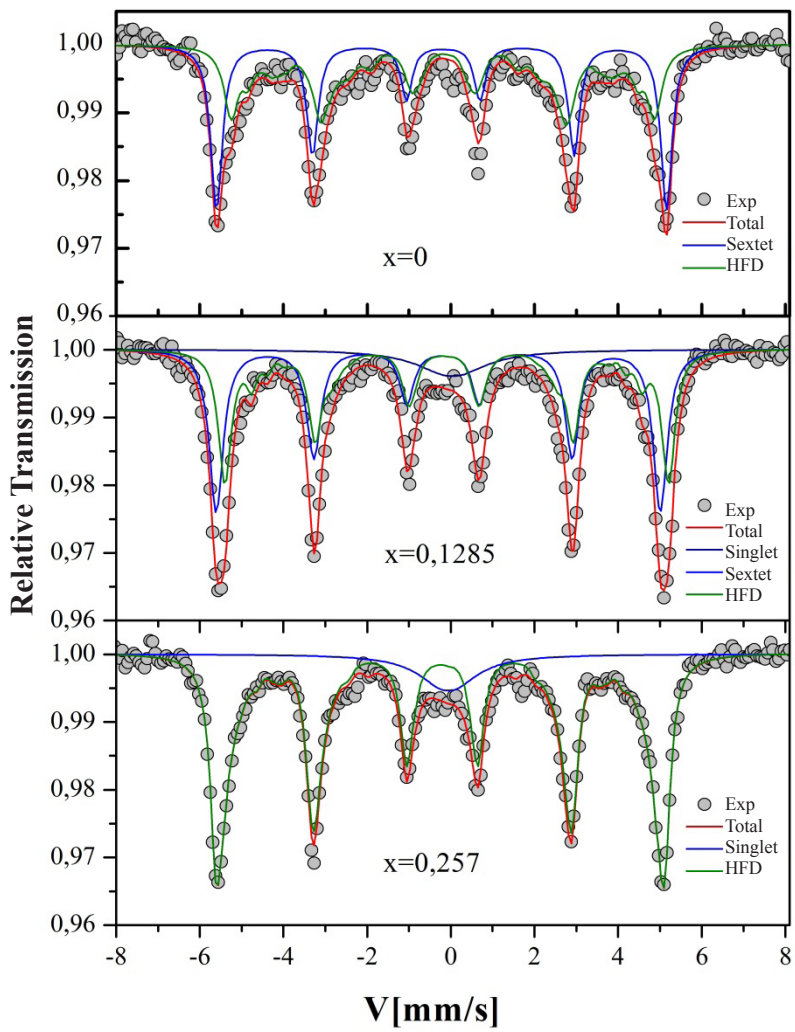
Sample	Phases	Network parameters ± 0.001 (Å)	Crystallite size(nm)	Volume fraction
$Gd_{0.257}Fe_{0.743}$	Fe	a=2.866	12 ± 0.5	66
	Fe_5Gd	a=4.634 c=4.145	45 ± 5	5
	GdN	a=4.944	6 ± 0.5	29
$Gd_{0.1285}Nd_{0.1285}Fe_{0.743}$	Fe	a=2.870	12 ± 0.3	22
	Fe_5Gd	a=4.746 c=3.930	5 ± 0.4	14
	Fe_5Nd	a=4.516 c=4.401	15 ± 2	4
	GdN	a=5.138	3 ± 0.1	15
	$Nd(OH)_3$	a=5.882 c=3.924	3 ± 0.1	40
	GdH_2	a=5.432	10 ± 1	5
$Nd_{0.257}Fe_{0.743}$	Fe	a=2.862	9 ± 0.2	44
	Fe_5Nd	a=4.741 c=4.342	5 ± 0.6	9
	NdN	a=5.061	7 ± 0.2	16
	Nd_2O_3	a=3.825 c=6.150	3 ± 0.1	31

Figure 2 shows the Mössbauer spectra at room temperature for the system $Gd_{0.257-x}Nd_xFe_{0.743}$ with x=0, 0.1285 and 0.257, milled for 72 hours, and **Table 2** presents the Mössbauer parameters: hyperfine field (B_{HF}) in teslas, isomeric shift (δ), line width (Γ) and quadrupole splitting (Δ) in *mm/s*, all corresponding to each component with which the Mössbauer spectra of the system were fitted. The Mössbauer spectrum corresponding to composition x=0 was fitted with two components: a sextet with an HF of 33.2 T and an HFD with a majority spectral area of 54%. According to the XRD results, the sextet can be associated with the α-Fe phase and the HFD to the Fe_5Gd phase, as reported by Novy et al. (1961) and Zhang et al. (1998). The spectrum corresponding to the composition x=0.1285 was fitted with three components: component (i) with a paramagnetic phase corresponding to a singlet with a spectral area of 9%, associated with Fe sites with Nd atoms as nearest neighbors, another component (ii) with a sextet with an HF of 33.7 T and a majority spectral area of 46% attributed to the existence of α-Fe sites and a component (iii) with an HFD with a spectral area of 45% associated with the subnetwork of Fe_5Gd; as can be seen in the results of XRD. The spectrum corresponding to the composition x=0.257 was fitted with two components: a paramagnetic phase corresponding to a singlet with a spectral area of 10%, associated with Fe sites with Nd atoms as nearest neighbors and an HFD with a spectral area of 90% associated with sites rich in α-Fe.

TABLE 2. MÖSSBAUER PARAMETERS OF THE SYSTEM $GD_{0.257-X}ND_XFE_{0.743}$ WITH X=0, 0.1285, 0.257, MILLED FOR 72 HOURS

Sample	Component	δ (*mm/s*) ± 0.001	Γ (*mm/s*) ± 0.001	Δ (*mm/s*) ± 0.001	B_{HF} (T) ± 0.1	%
$Gd_{0.257}Fe_{0.743}$	Sextet	0.004	0.163	-0.041	33.2	46
	HFD	---			30	54
$Gd_{0.1285}Nd_{0.1285}Fe_{0.743}$	Singlet	0.233	0.945	---	---	9
	Sextet	-0.243	0.202	-0.111	32.7	46
	HFD	---			29.3	45
$Nd_{0.257}Fe_{0.743}$	Singlet	0.177	0.775	0.003	-----	10
	HFD	---			28	90

Figure 2. MS of system $Gd_{0.257-x}Nd_xFe_{0.743}$ with x=0, 0.1285, 0.257, milled for 72 hours



4. CONCLUSIONS

$Gd_{0.257-x}Nd_xFe_{0.743}$ milling powders were obtained and studied by mechanical alloying with x = 0, 0.1285, 0.257 with a milling time of 72 hours. The samples obtained with the given conditions behave as a ferromagnetic system.

Samples $Gd_{0.257}Fe_{0.743}$ and $Gd_{0.1285}Nd_{0.1285}Fe_{0.743}$ present a ferromagnetic phase which indicates that the Gd atoms favor the magnetic order of Fe, but not the $Nd_{0.257}Fe_{0.743}$ and $Gd_{0.1285}Nd_{0.1285}Fe_{0.743}$ samples, which reveal paramagnetic iron sites, indicating that Nd atoms affect the magnetic order of iron.

With the substitution of the Gd atoms for the Nd atoms, the magnetic order is affected in such a way that iron sites showing magnetic disorder appear.

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