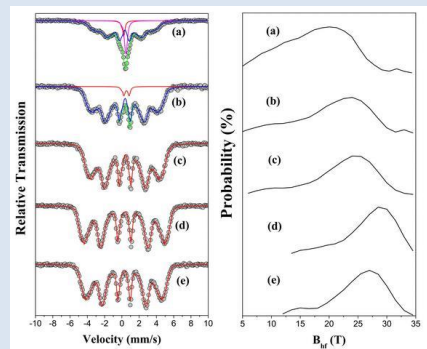


EFFECT OF HEAT TREATMENT ON THE STRUCTURAL AND MAGNETIC PROPERTIES OF THE SYSTEM $\text{Fe}_{56.25}\text{Al}_{43.75}$ PREPARED BY MECHANICAL ALLOYING

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ABSTRACT

The study of the $\text{Fe}_{56.25}\text{Al}_{43.75}$ system prepared by Mechanical Alloying (MA), using elementary powders, at milling times of 12, 24, 48, 72, and 96 hours, named MA0 samples, showed that the alloy is consolidated at 48 hours. Samples that were consolidated at this time were heat treated. This procedure consisted in heating the encapsulated specimens in quartz tubes under inert atmosphere conditions (Ar gas) at 700 °C for 9 days in a furnace. After this time, the samples were mechanically alloyed for times ranging from 1 to 48 hours. These samples, named MA1, were studied using Mössbauer Spectrometry (MS) and (X-Ray Diffraction) XRD aiming to obtain information on their magnetic and structural properties. XRD results of MA0 samples allow us to prove that they are nanostructured with a single FeAl BCC disordered phase with an approximately constant lattice parameter of 2.900 Å, and crystallite size which decreases with the increase of milling time. For the MA1 samples XRD results show that they exhibit some degree of ordering. The X-ray diffraction spectra allow to identify the FeAl, Fe_3Al , FeO and $\alpha\text{-Fe}$ phases. All the phases tend to disappear except the FeAl phase. The MS results of the MA0 samples prove that the FeAl phase is ferromagnetic. An increase of the mean hyperfine field (MHF) was found due to the increase of the structural disorder induced by the MA process. From MS of MA1 samples it was found that for times of 0, 1, 4, 8, and 12 hours, there is a disordered tendency and it was necessary to add a doublet, associated to paramagnetic sites of the FeAl phase, in order to obtain a better fit. Likewise for milling times of 24 and 48 hours, the doublet was changed by another which is associated with the FeO phase (wüstite), maybe due to an oxidation promoted by a leak in the seal of the jars.

Palabras Claves: Mössbauer spectroscopy, X ray diffraction, Mechanicals alloying, Nanostructure material

EFECTO DEL TRATAMIENTO TERMICO SOBRE LAS PROPIEDADES MAGNETICAS Y ESTRUCTURALES DEL SISTEMA $\text{Fe}_{56.25}\text{Al}_{43.75}$ PREPARADO POR ALEAMIENTO MECANICO

RESUMEN

El estudio del sistema $\text{Fe}_{56.25}\text{Al}_{43.75}$ preparado por aleamiento mecánico (AM), utilizando polvos elementales, a tiempos de molienda de 12, 24, 48, 72 y 96 horas, llamadas muestras MA0, muestran que la aleación se consolida a 48 horas. Las muestras que fueron consolidadas a este tiempo fueron tratadas térmicamente. Este procedimiento consistió en calentar los especímenes encapsulados en tubos de cuarzo en atmósfera inerte (gas Ar) a 700 °C durante 9 días en un horno. Después de este tiempo, las muestras fueron mecánicamente aleadas para tiempos entre 1 y 48 horas. Estas muestras, llamadas MA1, fueron estudiadas por Espectrometría Mössbauer (EM) y Difracción de Rayos-X (DRX) con el objetivo de obtener información de sus propiedades magnéticas y estructurales. Los resultados de DRX de las muestras MA0 nos permiten probar que ellas son nanoestructuradas con solo la fase FeAl BCC desordenada, con un parámetro de red aproximadamente constante de 2.900 Å, y un tamaño de cristalito que decrece con el incremento del tiempo de molienda. Para las muestras MA1 los resultados DRX muestran que ellas exhiben un cierto grado de orden. Los espectros de DRX permiten identificar las fases FeAl, Fe_3Al , FeO y $\alpha\text{-Fe}$. Todas las fases tienden a desaparecer excepto la FeAl. Los resultados de EM de las muestras MA0 prueban que la fase FeAl es ferromagnética. Se encontró un aumento del campo hiperfino medio (CHM) debido al aumento del desorden estructural inducido por el proceso de AM. Por EM de las muestras MA1 se encontró que para tiempos de 0, 1, 4, 8, y 12 horas, existe una tendencia al desorden y fue necesario agregar un doblete, asociado a los sitios paramagnéticos de la fase FeAl, con el fin de obtener el mejor ajuste. Sin embargo para tiempos de molienda de 24 y 48 horas, el doblete fue cambiado por otro que fue asociado con la fase FeO (wüstite), tal vez debido a la oxidación promovida por fallas en la sellada de las jarras.

Keywords: Espectroscopia Mössbauer, Difracción de rayos X, Aleamiento mecánico, Material nanoestructurado.

1. INTRODUCTION

The Fe-Al binary alloy had been studied during many years due to its wide range of magnetic and structural properties and its potential industrial applications. Magnetic properties are mainly related to their structural ordering; i.e. some alloys prepared by mechanical alloying (MA) show an increment in the ferromagnetic behavior associated to the induced disorder [1-4]. Ordered samples with concentrations higher than 33 at. % Al, normally exhibits a paramagnetic behavior, however they behave as ferromagnetic when they are disordered by MA [1-4]. An increment in the lattice parameter had been found too, attributed to the higher size of the Al atom against the Fe atom size [5]. Commonly, a reduction of the crystallite sizes and an increment of the internal strain are found too, when milling time increases [5, 6]. Moreover, the crystallite size increases and the internal strain reduce when a heat treatment is performed [5, 6]. As the FeAl alloy is thermally treated a change in the structure of the alloy and a paramagnetic site associated with the increase in thermally induced order are found [7].

In this work, we present a study of the $\text{Fe}_{56.25}\text{Al}_{43.75}$ system prepared by mechanical alloying, using elementary powders, at different times (12, 24, 48, 72 and 96 hours), named MA0 samples. It was found that the alloy is consolidated at 48 hours. Taking the sample for this time, a structural and magnetic study was conducted using Mössbauer spectrometry (MS) and X-ray diffraction (XRD). The consolidated sample of 48 h was synthesized by a thermal treatment at 700°C and mechanically alloyed again during alloying times of 1, 4, 8, 12, 24 and 48 h (MA1 samples) and XRD and MS experiments were performed. We selected this composition because it corresponds to the B32 super lattice structure and their magnetic properties are easy simulated by the Monte Carlo method.

2. EXPERIMENTAL METHOD

$\text{Fe}_{56.25}\text{Al}_{43.75}$ powdered sample was mixed using highly pure fine powders ($\geq 99.90\%$) of Fe and Al. From this sample it was selected different powders which were MA at milling times of 12, 24, 48, 72 and 96 hours, respectively. The milling took place in a high energy planetary mill Fritsch - Pulverisette 5. The grinding was performed in jars with stainless chrome steel with balls of the same material inside,

an jars were evacuated until 5.7×10^{-2} mbar, and the ratio of balls to powder mass was 20:1. The MA was performed with a sequence of 1 hour milling and 1 hour pause. The sample milled during 48 h was selected for further heat treatment, considering that for this grinding time the alloy is homogeneous and the welding and fracturing process has reached its equilibrium state. Taking the sample for this time it was compacted at 1 ton, encapsulated in a filled with Ar quartz tube. Later heat treatment was performed at 700 °C for 9 days and then mechanically alloyed (1, 4, 8, 12, 24 and 48 hours). All the prepared samples were characterized with Mössbauer spectrometry and XRD measurements. Mössbauer measurements were performed in a constant acceleration spectrometer at room temperature with transmission geometry using a $^{57}\text{Co}(\text{Rh})$ source of 25 mCi. All spectra were fitted with the Mosfit program and the isomeric deviation values were referred to $\alpha\text{-Fe}$. The X-ray measurements were obtained using Cu-K α radiation and the patterns were described using the Maud program, which is based in the Rietveld method combined with Fourier analysis to describe the broadening of the lines. This yielded the average values of the lattice parameter, crystallite size and the structural phase.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction results

XRD analysis shows, for all MA0 samples, a Fe-Al solid solution corresponding to a BCC structural phase with lattice parameter near 2.900 Å (Table 1). The XRD diffraction spectra of all samples are very similar, as it could be seen in Figure 1. XRD refinement by Rietveld method allowed us to get the crystallite sizes for the different products in according to the alloying time. The values for the crystallite sizes are included in Table 1. The values range from minimum of 133 Å for the sample milled during 96 h, up to the highest of 164 Å for the sample milled during 24 h, which corresponds to the second alloying time. It is clear that alloying time has an important role in this parameter.

In Figure 2 we show the XRD diffraction spectra for the synthesized MA1 samples. It is included the as-produced one (0 h of heat treatment or 48 h of milling) for comparison.

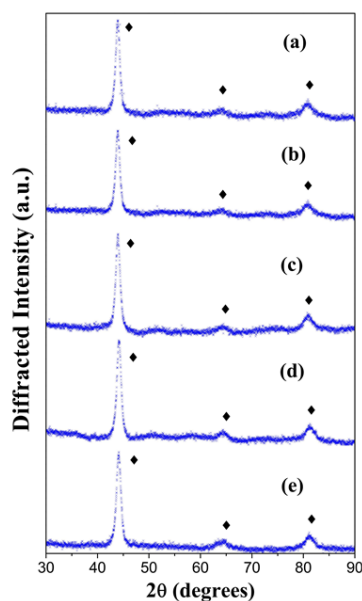


Figure 1. XRD diffraction spectra of $Fe_{56.25}Al_{43.75}$ MA0 samples, showing the FeAl (BCC) (◆) peaks milled for: (a) 12 h; (b) 24 h; (c) 48 h; (d) 72 h; and (e) 96 h.

Table 1. Structural parameters: lattice parameter (a) and crystallite size of MA0 samples.

Structural Parameter		
Time [h]	$a \pm 0.005$ [Å]	Crystallite Size (± 0.5) [nm]
12	2.910	16.1
24	2.898	16.4
48	2.910	15.1
72	2.903	15.7
96	2.899	13.3

It is evident, that for samples until 12 h the XRD diffraction spectra are very similar and the XRD analysis allows us to identify the simple cubic (SC) FeAl, Fe_3Al , FeO and α -Fe phases. Also, some additional diffraction peaks are present that could not be associated to a known crystallographic reported phase, but we tentatively associate them to the ϵ phase which appears in the Fe-Al metallurgical binary diagram [8], because this phase is within the range of composition of the sample and is stable at high temperatures and the heat treatment was conducted at this range of temperatures. From the XRD diffraction spectra corresponding to 24 h it is apparent that some peaks vanish and for 48 h the α -Fe BCC phase is the only one remaining. It is

attributed to the disorder induced by the milling time increase, very similar to the result obtained when sample was mechanically alloyed using elemental powders only (MA0 samples).

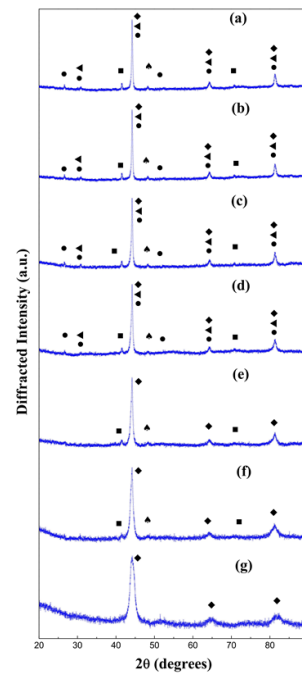


Figure 2. XRD diffraction spectra of $Fe_{56.25}Al_{43.75}$ MA1 samples, showing the Fe_3Al (●), α -Fe (◆), FeO (■), FeAl (▲), ϵ Phase (♠), peaks: (a) heated to $700^\circ C$; (b) milled for 1h and heated to $700^\circ C$; (c) milled for 4h and heated to $700^\circ C$; (d) milled for 8h and heated to $700^\circ C$; (e) milled for 12h and heated to $700^\circ C$; (f) milled for 24h and heated to $700^\circ C$; (g) milled for 48h and heated to $700^\circ C$.

3.2 Mössbauer results

Figure 3 shows the Mössbauer spectra of the alloyed MA0 samples using elemental powders. It is evident that they exhibit a ferromagnetic behavior with broad lines, showing their disordered character, in according with the results of Gialanella et al. [1]. All the MS spectra were fitted with a hyperfine magnetic field distribution (HMFD), and for those of the 12 and 24 h it was necessary to add a paramagnetic line (a doublet and a singlet for 12 h and a doublet for 24 h) attributed to Fe sites rich in Al of the FeAl phase. For 48, 72, and 96 h the spectra are ferromagnetic with and increasing MHF, which is due to the increase of the structural disorder induced by the MA favoring the ferro-ferro interactions confirming results previously pointed [1-3].

Table 2 shows the Mossbauer parameters obtained

for the MA0 samples and it can be noted a decrease of the isomer shift and an increase of the mean hyperfine field with the milling time, respectively, associated with the disorder generated by the MA. These results are in accordance to that of Zamora et al. [9] and Kobeissi [10]. This disorder contributes to the homogenization of the sample increasing in this way the mean number of Fe atoms around the Fe site and the microscopic consequence is the

increase of the mean number of *s* electron in the Fe nucleus. The increase of the ferromagnetic character is noted in the mean hyperfine field values which change from 22 to 28 T. The presence of the paramagnetic sites for samples milled during 12 and 24 h was reported by Bohorquez et al. [11] in Fe-Al disordered samples obtained by melting. The doublet parameters, $\Delta = 0.14 \text{ mm s}^{-1}$ and $\Gamma_{\text{exp}} = 0.32 \text{ mm s}^{-1}$ are very similar to those reported by them.

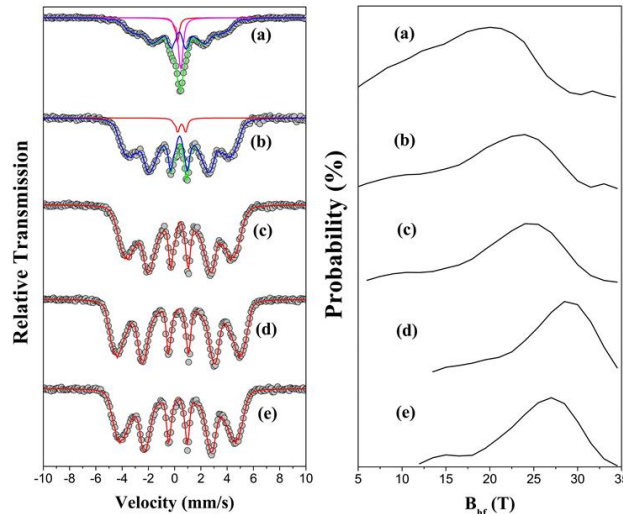


Figure 3. Mössbauer spectra (*left*) and corresponding hyperfine field distribution (*right*) for the same samples as in Figure 1.

Table 2. Hyperfine parameters: isomer shift (IS), mean hyperfine field $\langle B_{\text{hf}} \rangle$, quadrupole splitting (QS) of the Mössbauer spectra of Figure 3.

Hyperfine Parameter				
Time [h]	Component	$\langle B_{\text{hf}} \rangle \pm 0.2$ [T]	IS ± 0.05 [mm/s]	QS ± 0.05 [mm/s]
12	Singlet	---	0.01	0.14
	Doublet	---	0.26	
	Distribution	16.9	0.13	
24	Doublet	---	0.27	0.57
	Distribution	20.2	0.12	
48	Distribution	22.2	0.11	
72	Distribution	26.7	0.08	
96	Distribution	25.1	0.09	

Figure 4 presents the Mössbauer spectra for the MA1 samples. For the 0 h an ordering is evident because the lines are narrower. After 1 h of milling it seems that some degree of disorder is induced. The spectra fitting was performed with a doublet and a HMF.

In Table 3 are shown the obtained Mössbauer parameters for MA1 samples. It can be noted that the mean hyperfine field increase with the milling time, and this is again associated to the disorder generated by MA. It was necessary to add a paramagnetic site to fit the spectra for 0, 1, 4, 8, and

12 h. This is a doublet with $\Delta = 0.48 \text{ mm s}^{-1}$ and $\Gamma_{\text{exp}} = 0.50 \text{ mm s}^{-1}$, and for the spectra of 24 and 48 the doublet presents $\Delta = 0.95 \text{ mm s}^{-1}$ and $\Gamma_{\text{exp}} = 0.30 \text{ mm s}^{-1}$. The doublet obtained for samples milled up to 12 h is associated to the ordered FeAl single phase, detected by XRD. This phase is induced by the thermal treatment as was also discussed by

Zamora et al. [7]. The doublet which appears at 24 y 48 h is associated to the FeO phase (wüstite). The Mean Hyperfine Field ranges from 16 T corresponding to the pure synthesized sample up to 23 T. These values are smaller than that obtained for the MA0 samples.

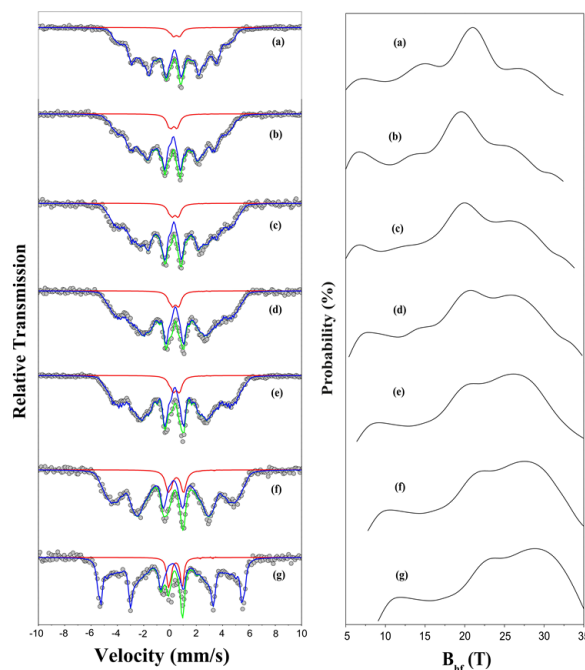


Figure 4. Mössbauer spectra (*left*) and corresponding hyperfine field distribution (*right*) for the same samples as in Figure 2.

Table 3. Hyperfine parameters: isomer shift (IS), mean hyperfine field $\langle B_{\text{hf}} \rangle$, quadrupole splitting (QS) of the Mössbauer spectra of Figure 4.

Time [h]	Component	Hyperfine Parameter		
		$\langle B_{\text{hf}} \rangle \pm 0.2$ [T]	IS ± 0.05 [mm/s]	QS ± 0.05 [mm/s]
0	Doublet	---	0.33	0.48
	Distribution	17.5	0.19	
1	Doublet	---	0.23	0.48
	Distribution	18.0	0.17	
4	Doublet	---	0.27	0.48
	Distribution	19.5	0.21	
8	Doublet	---	0.15	0.48
	Distribution	20.9	0.13	
12	Doublet	---	0.26	0.48
	Distribution	22.0	0.17	
24	Doublet	---	0.28	0.95
	Distribution	25.3	0.08	
48	Doublet	---	0.28	0.95
	Distribution	27.6	0.21	

4. CONCLUSIONES

XRD results of all MA0 samples show a Fe-Al solid solution corresponding to a BCC structural phase, with lattice parameter close to 2.900 Å. Additionally, their XRD analysis showed a decrease in crystallite size associated with the increase of the milling time. For the MA1 samples the results show that until 12 h the thermal treatment induce a change in structure and phases: the simple cubic (SC) FeAl, the Fe₃Al, the FeO, Fe-Al BCC and the ε phases are now present. For the sample corresponding to 24 h it is apparent that some peaks vanish and for 48 h the Fe-Al BCC phase is the only one which appears, and this is attributed to the disorder induced by the increase of the milling time, very similar to the result obtained when sample was mechanically alloyed using elemental powders only. Mossbauer spectrometry study of the MA0 samples showed a decrease of the isomer shift and an increase in the mean hyperfine field with the milling time associated with the disorder generated by the MA. This disorder contributes to the disappearing of the two paramagnetic sites obtained after the heat treatment and to the increase of the mean hyperfine field with the increase of the milling time. For 24 h and 48 h milling time a doublet with $\Delta = 0.95 \text{ mm s}^{-1}$ and $\Gamma_{\text{exp}} = 0.30 \text{ mm s}^{-1}$ associated to the appearing of a Fe oxide of the FeO type.

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