Structural and hyperfine study of the \((\text{Fe}_{60}\text{Al}_{40})_{100-x}\text{Nb}_x\) nanostructured system

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A study was made by x-ray diffraction and Mössbauer spectroscopy of the structural and hyperfine properties of the \((\text{Fe}_{60}\text{Al}_{40})_{100-x}\text{Nb}_x\) system, with \(x = 5, 10, 15\) and 20 \% at. Nb. The samples were obtained by mechanical alloying in a high energy planetary mill, with milling times of 12, 24, 36 and 72 hours. From the refinement of x-ray patterns, the lattice parameter and grain size were obtained. Two phases were necessary to refine these spectra, one associated with the bcc (Fe-Al) phase, and the other one associated to a hexagonal (FeAl)\(_2\)Nb phase. The lattice parameter of the bcc phase increases with the Nb content from 2,922 to 2,986 Å for 12 hours milling and a similar behavior was obtained for the other milling times. The hexagonal phase is present in samples with \(x=10, 15\) and 20, with lattice parameters \(a=4.887\) Å and \(c=7.897\) Å for 12 hours milling. This phase tends to disappear when the milling time increases. The grain size changes from 20 to 2 nm, but does not show any specific trend, however these values show that this system is nanostructured. From the Mössbauer spectra, two components were necessary in order to fit the \(x=5\) sample to obtain the fit, one paramagnetic component (singlet) and one magnetic hyperfine field distribution (MHFD). The MHFD spectral area increases with the increase of the milling time, and the mean hyperfine field changes from 16.6 to 23.5 T. This behavior is attributed to the increase of the structural disorder induced by the mechanical alloying. The samples with other concentrations, namely \(x=10, 15\) and 20, are paramagnetic. For these samples the mechanical milling does not induce a magnetic behavior due to the substitution of Fe by Nb atoms. However for the sample with \(x=15\) and 24 hours of milling it was possible to induce a magnetic behavior, after a heat treatment at 1000°C for 1 day, and the magnetic component present a mean hyperfine magnetic field of 22.3 T.

**Keywords:** Fe-Al alloys; Fe-Nb alloys, mechanical alloying; X-rays diffractions; Mössbauer spectroscopy.

Se realizó un estudio sobre las propiedades estructurales e hiperfina por difracción de rayos X y espectroscopia Mössbauer, respectivamente, sobre el sistema \((\text{Fe}_{60}\text{Al}_{40})_{100-x}\text{Nb}_x\) (con \(x = 5, 10, 15\) y 20\% menos. Nb). Las muestras se obtuvieron por aleamiento mecánico en un molino planetario de alta energía, con tiempos de molienda de 12, 24, 36 y 72 horas. Desde el refinamiento de los espectros de rayos X, se obtuvieron el parámetro de red y el tamaños de grano. Dos fases fueron necesarias para refinar estos espectros, una asociada con la fase bcc (Fe-Al), y la otra asociada a una fase hexagonal (FeAl)\(_2\)Nb. El parámetro de red de la fase bcc aumenta con el contenido de Nb desde 2,922 a 2,986 Å para 12 horas de molienda y un comportamiento similar se obtuvo para los otros tiempos de molienda. La fase hexagonal está presente en las muestras con \(x=10, 15\) y 20, con parámetros de red a = 4,887 Å y c = 7,897 Å para 12 horas de molienda. Esta fase tiende a desaparecer al aumentar el tiempo de molienda. El tamaño de grano cambia de 20 a 2 nm, pero no muestra ninguna tendencia, sin embargo, estos valores muestran que este sistema es nanoestructurado. Para el ajuste las muestra con \(x = 5\), dos componentes fueron necesarias, una componente paramagnética (singlete) y una distribución de campo magnético hiperfino (DCMH). El área espectral de la DCMH incrementa cuando el tiempo de molienda aumenta, y el campo hiperfino medio cambia desde 16,6 a 23,5 T. Este comportamiento se atribuye al aumento del desorden estructural inducido por el aleamiento mecánico. Las muestras con otras concentraciones, es decir, \(x=10, 15\) y 20, son paramagnéticas. Para estas muestras la molienda mecánica no induce un comportamiento magnético debido a la sustitución de Fe por átomos de Nb. Sin embargo, para la muestra con \(x = 15\) y 24 horas de molienda, fue posible inducir un comportamiento magnético, después de un tratamiento térmico a 1000°C durante 1 día, y la componente magnética presenta un campo magnético hiperfino medio de 22,3 T.

**Descripciones:** Aleaciones Fe-Al; aleaciones Fe-Nb; aleamiento mecánico; difracción de rayos-X; espectrometría Mössbauer.

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1. Introduction

The Fe-Al alloys have been motive of study since several decades due of its wide spectrum of magnetic and structural properties. Experimental results have shown that this alloy produced by casting is ferromagnetic (F) for lower concentrations than 33 at. \% Al, and paramagnetic (P) above this concentration. The BCC structure is present until concentrations near 50 at. \% Al, and can be structurally ordered according to the heat treatment carried out [1-4]. It has been observed that the ferromagnetism in this alloy is associated with an increase in structural disorder and the lattice parameter. For example, for samples produced by mechanical alloying (MA) it was obtained F behaviour for concentrations above 33 at. \% Al, depending on milling time [5,6].

FeNb alloys present a special interest mainly for its applications in industry; however, they cannot be obtained by melting due to the difference between its casting temperature (1809 K for Fe and 2742 K for Nb). MA is an excellent choice for obtain alloys of these type. Studies made have shown that the alloy Fe\(_2\)Nb obtained through of casting techniques presents the C14 Laves phase, with an antiferromagnetic transition and a Neel temperature below 20 K [7-9]. On the other hand studies of Fe\(_{1-x}\)Nb\(_x\) alloys obtained by MA...
show that them are amorphous when the content of Nb as well as the milling time increase [10].

Addition of niobium in Fe-Al alloys produces an increase in tensions due to the formation of fine precipitates of the Laves phase (Fe-Al)$_2$Nb [11,12]. Recent studies concerning the Fe$_{54}$Al$_{36}$Nb$_{10}$ and Fe$_{48}$Al$_{32}$Nb$_{20}$System, with $x=10$ and 20, obtained by mechanical alloying, show that the milling time and composition play an important role on the magnetic and structural properties of the alloy, as well as the presence of superparamagnetism due to small crystallite size of the bcc phase (Fe, Al) and hcp (Fe, Al)$_2$Nb [13]. With the aim to complement this work, we performed DRX and Mössbauer study of this system in a wider range of concentrations (5, 10, 15 and 20), and milling times of 12, 24, 36 and 72 hours; and also the effect of heat treatment in the sample with $x=15$ and 24 hours of milling.

2. Experimental

Using highly pure fine powders ($\geq 99.8\%$) of Fe, Al and Nb, samples of the system (Fe$_{60}$Al$_{40}$)$_{100-x}$Nb$_x$ (with $x=5, 10, 15$ and 20 % at.) where prepared by MA, during milling times of 12, 24, 36 and 72 hours. Additionally the sample with $x=15$ at 24 hours of milling was heat treatment at $1000\,\degree\,C$ during 24 hours. For the milling, a high energy planetary ball mill Fritsch-Pulverisette 5 was used. The milling of the powders was performed in stainless steel jars with balls of the same material inside. The ratio between balls and powder masses was 15:1 and the speed was 280 rpm. The XRD and Mössbauer study were conducted at room temperature. The XRD was realized in a powder diffractometer with Co-K\textsubscript{α} radiation ($\lambda=1.7890$ Å) and they were refined by using the MAUD program [14]. Mössbauer spectra where taken on a conventional spectrometer with a $^{57}$Co/Rh source of 925 M bq. All the spectra were fitted with the MOSFIT program [15].

3. Results and discussion

Figure 1 shows the XRD pattern of the sample with $x=5$ alloyed during 12 hours of milling for other time the pattern are similar. From the fit of the XRD pattern it was found that the obtained lines correspond to the bcc $A_2$ phase (space group $I\overline{m}3m$). This result suggests that both the aluminum and niobium atoms diffuse into the bcc iron matrix. The obtained lattice parameter is 2.922 Å, which is slightly higher than the lattice parameter of the Fe$_{60}$Al$_{40}$ alloy obtained by MA (2.915 Å), (see Table I) [6]. This enhance of the lattice is due to the size of the aluminum and niobium atoms which are similar and larger than the size of the iron atom, then the replacement of Fe and Al by niobium atoms produce as a net effect an expansion of the lattice, however as the concentration of Nb is small, dilatation of the lattice is minimal. The structural behavior of MA samples during 24, 36 and 72 hours is similar to that presented by the sample alloyed for 12 hours.

The XRD patterns of samples with $x=10$ alloyed at different milling times can be seen in Fig. 2. It can be noted...
in this case that the increase in Nb concentration allows the formation of the hcp phase (Fe,Al)$_2$Nb with spatial group P4/nmm. After 36 hours milling this phase tends to disappear while the bcc phase (Fe,Al) transforms into the bcc phase (Fe,Al-Nb) and present a tendency to be disorder (only the principal line appears). As for $x = 5$, the lattice parameter of the bcc phase is bigger than that of Fe$_{60}$Al$_{40}$ alloy (see Table I). The explanation is analogous, only that in this case the alloy has a higher Nb content and therefore the dilatation of the lattice is more significant. Between 24 and 36 hours of milling the lattice parameter increases considerably, this behavior is due to the transformation of the bcc phase (Fe,Al) bcc in the phase (Fe,Al-Nb). Samples with $x = 15$ and $x = 20$ present similar behavior.

The values of the lattice parameter and of the crystallite size obtained from the refinement of different XRD patterns are reported in Table I. The crystallite sizes of the different samples vary between 2 and 19 nm, but there are not show any tendency with the Nb content neither with the milling time, however these results indicate that the system is nanostructured.

Figure 3 shows the Mossbauer spectra and their MHFDs for samples with $x = 5$. For 12 hours of milling the sample exhibits two phases: a majority P (singlet) and a small proportion of a F one (MHFD). When the milling time increases the P component decreases until it disappears at 72 hours of milling; in contrast, the F character of the sample increases. The same conclusion can be deduced through the MHFD: for 12 hours of milling in the MHFD predominates the smaller magnetic fields with low probabilities, when the milling time increases it appears a peak with higher probability which displaces to larger values of hyperfine magnetic field increasing in this way the mean value. The mean hyperfine field increases from 17.3 to 23.2 T, when the milling time increases from 12 to 72 hours, respectively. According to Table I, the lattice parameter for samples with $x=5$ remains constant which suggests that the increase in the F behavior depends only on the milling time, in other words, the ferromagnetism increases due to the increase of the structural disorder induced by the MA. This behavior is similar to that presented by the alloy FeAl obtained by MA [5,6], therefore the addition of 5 at. % Nb does not generate significant changes in the magnetic behavior of the alloy.

All of samples with $x = 10$, 15 and 20 obtained at different milling times presents a behavior P, and they present a Mossbauer spectrum similar to that of the alloy with $x = 15$ alloy and 24 hours milling shown in Fig. 4. The fit of the spectra was performed using a distribution of doublets, which indicates that the alloy is P and disordered [16], the spectra do not show the appearance of a F component with the increase of milling time, as well as observed in samples with $x = 5$. Two reasons are suggested to justify the absence of ferromagnetism: i) the low percentage of iron in the alloy (less than 53% at.) joined with the increase of Nb content and, ii) the F grains of the bcc phase (Fe, Al) do not interact each other because of their small size and low total moment and besides they are surrounded by P grains of the (Fe, Al)$_2$Nb phase.
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\section*{In order to examine the effect of heat treatment on the structural and hyperfine properties of the P samples, that with \(x = 15\) and milled during 24 hours was sintered at 1000°C during 24 hours. The XRD pattern and Mossbauer spectrum of the alloy after heat treatment are shown in Fig. 5. The structural disorder of the sample decreases as can be seen by the decrease of the peak width of the diffractogram (Fig. 5a). The structural bcc (Fe, Al) and hcp (Fe, Al)\(_2\)Nb phases are preserved. The structural parameters obtained from the refinement are listed in Table II. The lattice parameter of the bcc phase decreases slightly, while that of the hcp phase remains constant. As usual in the sintered process, the crystallite sizes of both phases increase from 5 to 27 nm and from 3 to 25 nm for the bcc and hcp phases, respectively. The Mossbauer spectrum of the heat treated sample (Fig. 5b) shows that the P component continues to prevail (doublet), but in this case it was necessary to add a MHFD with mean value of 22.3 T. This distribution is associated with the increase of the grains of the bcc F phase (Fe, Al). These grains present now a bigger magnetic moment permitting in this way that they correlate and behave as F. The fit of this contribution with a HMFD shows that the grade of disorder remains after the heat treatment.}

\begin{table}[h]
\centering
\caption{Structural parameters obtained from the refinement of XRD patterns of the alloy sintered at 1000°C.}
\begin{tabular}{ccc}
\hline
\textbf{x} & \textbf{Phase} & \textbf{Lattice parameter / 24 h Grainsize} \\
& & \textbf{\(a\pm0.005\) Å / \((t\pm2)\) nm} \\
15 & bcc & (7.904 / 27) \\
& hcp & (4.864 / 25) \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Mössbauer spectra and their respective hyperfine magnetic field distributions for the samples with \(x = 5\).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Mössbauer spectrum of the sample with \(x=15\) alloyed during 12 hours.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5}
\caption{a) XRD pattern and b) Mössbauer spectrum, of the sample with \(x=15\) alloyed during 24 hours and heat treated at 1000°C during 24 hours.}
\end{figure}
4. Conclusions

Samples of the \((\text{Fe}_{60}\text{Al}_{40})_{100-x}\text{Nb}_x\) system, with \(x = 5\), prepared by MA during 12, 24, 36 and 72 hours, present a single BCC (Fe, Al) phase. The addition of niobium does not make major changes in the binary alloy. In contrast for the other concentrations \(x = 10, 15\) and 20, niobium plays a significant role in these alloys. Two phases appear, the BCC (Fe,Al) and the hexagonal \((\text{Fe,Al})_2\text{Nb}\). Mossbauer spectra of sample with \(x = 5\) show the existence of ferromagnetism, which increases with milling time. For \(x = 10, 15\) and 20, they are P and the reason for the absence of F is that the F grains of the bcc phase (Fe, Al) do not interact among themselves due to their small size and magnetic moment and to the formations of P grains of the \((\text{Fe,Al})_2\text{Nb}\). With the heat treatment made to the sample with \(x = 15\) and 24 hours of milling it appears again the bcc (Fe, Al) phase which now is F with lest degree of disorder. The appearance of F is due to the increase in grain size, and then of its magnetic moment, produced by the process at which the sample was submitted.

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15. F. Varret and J Teillet.: Unpublished MOSFIT Program.