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Mössbauer and X-ray diffraction studies of nanostructured Fe₇₀Al₃₀ powders elaborated by mechanical alloying

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ABSTRACT

We have studied the effect of milling time on the structural and hyperfine properties of Fe₇₀Al₃₀ compound elaborated by mechanical alloying. The elaboration was performed with a vario-planetary ball mill P4 at different milling times. The milled powders were characterized by X-ray diffraction (XRD) and Mössbauer spectroscopy. From XRD diffraction spectra, we show that the bcc Fe(Al) solid solution was completely formed after 27 h of milling time. When the milling time increases, the lattice parameter increases, whereas the grain size decreases and the mean level of microstrains increases. The analysis of Mössbauer spectra shows that from 4 h of milling, a disordered ferromagnetic Fe₇₀Al₃₀ starts to form and dominates after 36 h.

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1. Introduction

Mechanical alloying has been successfully applied to elaborate Fe–Al systems with different compositions and it has been shown that different structures were formed, depending on milling conditions [1,2]. In fact, many works have reported the elaboration of nanocrystalline FeAl under different experimental conditions [3–11]. Among FeAl systems produced by mechanical alloying, nanocrystalline Fe₇₀Al₃₀ alloy have been the subject of various studies. For instance, Zamora et al. [12] investigated the effect of milling time (12, 24 and 36 h) on the crystallite size, lattice parameter and hyperfine magnetic field of Fe₇₀Al₃₀ powder mixture. According to their results, with increasing milling time, the lattice parameter remained constant but the crystallite size increased. The authors also followed the formation of Fe₇₀Al₃₀ powder versus milling time by Mössbauer spectroscopy. They showed that for all milling times, the Mössbauer spectra clearly indicated the existence of disordered ferromagnetic structure. In addition, Lozano et al. [13] studied the effect of milling time (12, 24, 36 and 48 h) on the structural and hyperfine properties obtained by X-ray diffraction and Mössbauer spectroscopy. According to their investigation, the mean grain size and the lattice parameter remain nearly constant with the milling time. Also, from the Mössbauer spectra, they

evidenced the disordered ferromagnetic character of the alloys for all milling times. E. Jartych [14] investigated the structural evolution of nanocrystalline Fe₇₀Al₃₀ compound as a function of milling time (up to 800 h). As their results showed, the crystallite size decreased and the lattice strain increased with milling time. They also followed the alloy formation by Mössbauer spectroscopy and they showed that after 800 h of milling time only ferromagnetic arrangement is present in the material.

In the present work, we reported on the effect of milling time on the structural and hyperfine properties of Fe₇₀Al₃₀ nanostructured powder elaborated by high energy ball milling. The evolution of structure and hyperfine properties will be studied by means of X-ray diffraction and Mössbauer spectroscopy.

2. Experimental

Elemental Fe and Al powders of 99.99% purity and particle sizes smaller than 100 μm were separately weighted and mixed to get the desired composition. The mechanical alloying process was performed in a vario-planetary high-energy ball mill (Fritsch P4). The ball-to powder weight ratio was 15:1. The rotation speed of the disc, Ω, and the vials, ω, were equal to 250 rpm and 400 rpm, respectively. Different milling times ranging from 4 to 48 h were used. X-ray investigations were performed using a Philips X'Pert Pro diffractometer in continuous scanning mode with Cu Kα radiation. The X-ray patterns were analyzed with the HighScore Plus software [15]. Each peak was fitted by a pseudo-Voigt (PV) function which is a linear combination of a Lorentzian (L) and a Gaussian (G) function: $PV(2\theta) = \gamma L(2\theta) + (1 - \gamma)G(2\theta)$ where γ is a refinable "mixing" parameter called shape parameter which describes the amount of Gaussian profile versus the amount of Lorentzian profile [15]. After removing the CuKα₂ radiation from the profiles by using the Rachinger method, the lattice parameter was calculated taking into account the most intense X-ray

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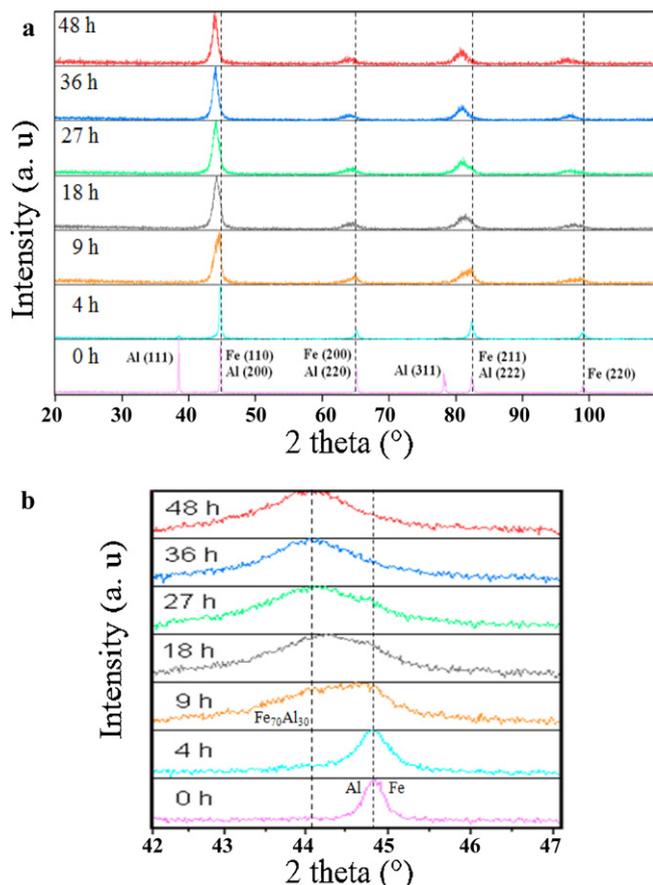


Fig. 1. (a) X-ray diffraction patterns of the $\text{Fe}_{70}\text{Al}_{30}$ powders milled for different milling times. (b) Deconvolution of the most intense peak for different milling time.

diffraction peaks of bcc-Fe and bcc-Fe(Al) phases (before and after the total formation of Fe(Al) solid solution, respectively). For the calculation of the mean grains size, $\langle D \rangle$, and mean level of microstrains, $\langle \epsilon \rangle$, the physical breadths β were determined from X-ray diffraction peaks.

The mean grains size, $\langle D \rangle$, was calculated according to Scherrer's formula included in the software and defined by [16]:

$$\langle D \rangle = K \cdot \frac{\lambda}{\beta_L} \cos \theta \quad (1)$$

where K represents the shape factor which varies with crystal shape, λ is the wavelength of the $\text{Cu K}\alpha_1$ radiation, θ is the Bragg angle and β_L is the breadth of the Lorentzian contribution to the peak, which has its origin in the reduced size of the grains. The average microstrain, $\langle \epsilon \rangle$, on the other hand, was calculated by using the tangent formula included in the software and given by [17]:

$$\langle \epsilon \rangle = \frac{\beta_G}{4 \tan \theta} \quad (2)$$

where β_G is the breadth of the Gaussian contribution to the peak, which has its origin in the presence of microstrains.

Mössbauer spectra were collected with a Wissel setup working in the constant acceleration mode. The spectra were adjusted with the Recoil software using the Voigt-based hyperfine field distribution method (HFD-VB-F).

3. Results

3.1. X-ray diffraction

Fig. 1a shows the X-ray diffraction patterns of $\text{Fe}_{70}\text{Al}_{30}$ samples after different milling times. X-ray diffraction spectrum for the starting mixture powder (labeled 0 h in Fig. 1a), shows the reflections corresponding to distinct bcc α -Fe and fcc Al peaks, where the Al (2 0 0), (2 2 0) and (2 2 2) peaks overlap with the Fe (1 1 0), (2 0 0) and (2 1 1) peaks, respectively. After 4 h of milling, the intensity of Al peaks decreases dramatically, however, one can still see the

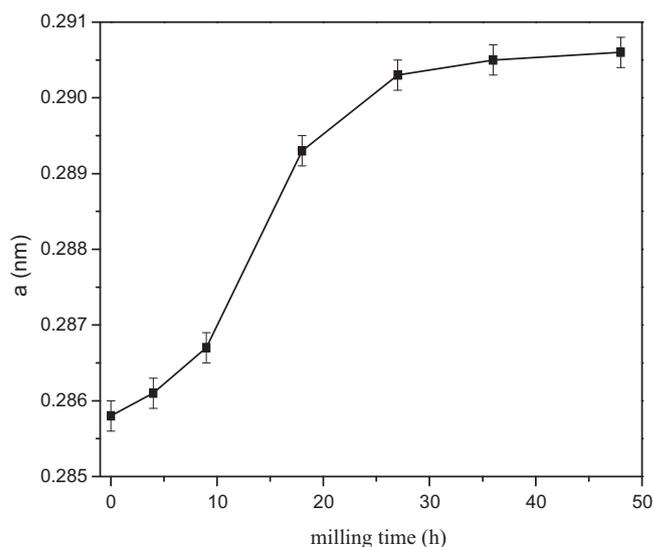


Fig. 2. Variation of lattice parameter a (nm) with milling time for the $\text{Fe}_{70}\text{Al}_{30}$ samples.

presence of Al (1 1 1) peak. This decrease of the intensity of Al peaks is generally attributed to the beginning of the formation of FeAl compound [7,8]. However, because of the limit detection of X-ray diffraction technique, it was difficult to conclude that the FeAl compound has started to form after 4 h of milling. After 9 h of milling, the beginning of the formation of a new phase is clearly seen from the asymmetry of the α -Fe peaks. Indeed, this asymmetry is traduced by the appearance, in XRD spectra, of a second peak located at the left side of α -Fe peaks. This peak increases in intensity with increasing milling time and dominates after 18 h. In order to identify the nature of this peak, we performed a deconvolution of the most intense XRD peak by using the HighScore Plus software (Fig. 1b). By comparing the peaks position to the JCPDS files included in the database of the software, we identify the new peak as the one characteristic of bcc Fe(Al) solid solution. Moreover, after 27 h of milling, a complete shift of X-ray diffraction peaks towards the lower angles is observed. This shift indicates that the Fe(Al) solid solution is completely formed [9,18].

Fig. 2 presents the change of lattice parameter (a) versus milling time (t) for $\text{Fe}_{70}\text{Al}_{30}$ samples. As the milling time increases and

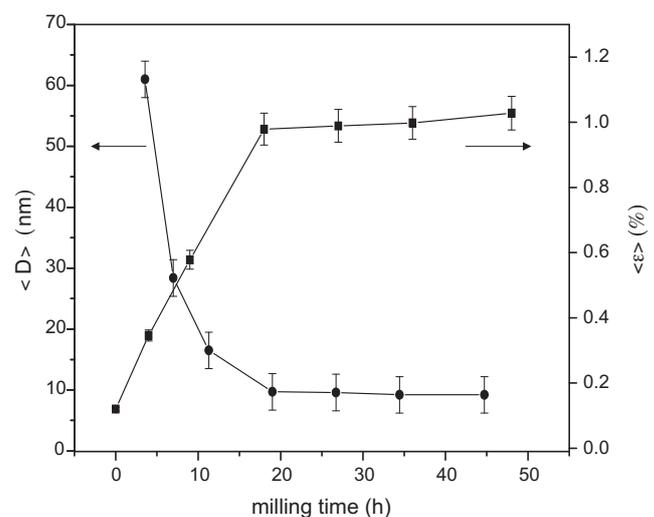


Fig. 3. Average crystallite sizes, $\langle D \rangle$ (nm), and mean internal strain, $\langle \epsilon \rangle$ (%), of $\text{Fe}_{70}\text{Al}_{30}$ powders versus milling time.

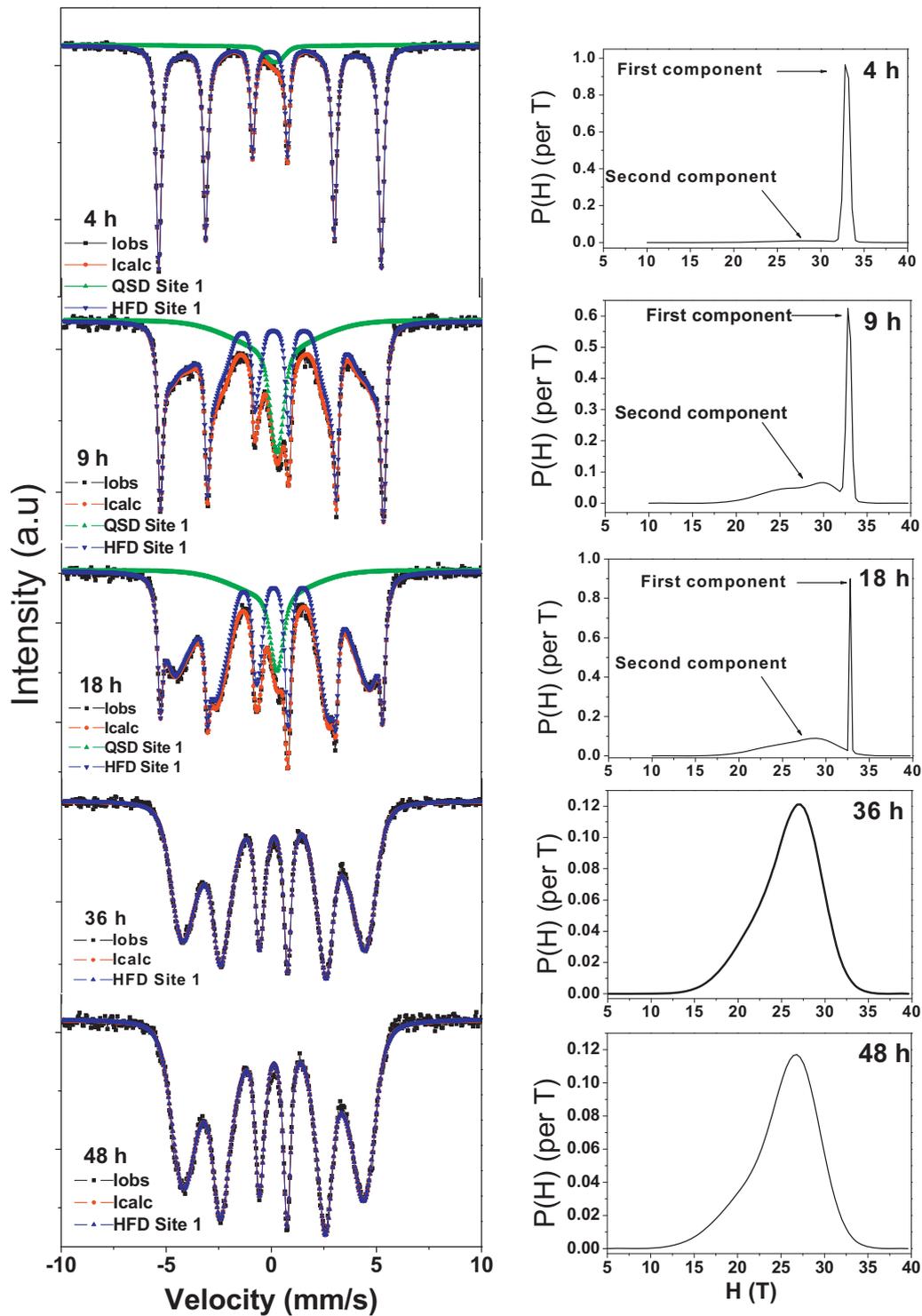


Fig. 4. Room-temperature Mössbauer spectra of $Fe_{70}Al_{30}$ for various milling times and their corresponding hyperfine field distribution obtained from the fitting of the spectra.

due to more Al diffusion, the lattice parameter increases from 0.2858 ± 0.0003 nm for the pure Fe to 0.2907 ± 0.0003 nm after 48 h of milling. Generally, the increase of lattice parameter with milling time is due to the solid solution formation. Moreover, in nanostructured materials produced by mechanical alloying, the increase of lattice parameter may also be due to the defects introduced in the interfaces. Indeed, the less dense structure of interfaces can result in some negative pressure on the interfaces as suggested by Zeng et al. [19] and this can lead to an increase in the lattice parameter.

For the longest milling time (48 h), the obtained value of the lattice parameter is in good agreement with those found by many authors [14,20].

Fig. 3 shows the evolution of the mean grain sizes, $\langle D \rangle$ (nm), and the mean level of microstrains, $\langle \epsilon \rangle$ (%), versus milling time. It can be seen that beyond 27 h of milling time, the grain sizes (mean level of microstrains) decreases (increases) quickly with increasing milling time. After 18 h of milling, the variations of $\langle D \rangle$ (nm) and $\langle \epsilon \rangle$ (%) are less pronounced. For the longest milling time (48 h), the

values achieved for $\langle D \rangle$ and $\langle \varepsilon \rangle$ are equal to 9 ± 1 nm and 1.028%, respectively. It is interesting to note that the final value of $\langle D \rangle$ (9 nm) achieved in this work is comparable to the one found by Eelman et al. [21] (10 nm) after 36 h using a Spex 8000 mill and is smaller than the one obtained by Zamora et al. [12] (28 nm) after 36 h of milling using a Pulverisette 5 high energy ball mill.

3.2. Mössbauer spectroscopy

The Mössbauer measurements were performed in order to monitor the process of alloy formation at every stage of milling. The room temperature Mössbauer spectra and the corresponding hyperfine field distributions for the samples milled for 4, 9, 18, 36 and 48 h are shown in Fig. 4.

In the first hours of milling (4 h), the Mössbauer spectrum was adjusted with a quadrupole doublet and one sextet. The quadrupole doublet, which disappears for milling time above 18 h, is explained by the formation of a paramagnetic phase rich with Al [8,22]. Concerning the sextet, it contains two components with $\langle H_{\text{hf}} \rangle$ equal to 32.9 T (96%) and 29 T (4%). The first component is typical of α -Fe and the second one is characteristic of the disordered ferromagnetic Fe(Al) solid solution with a composition of $\text{Fe}_{70}\text{Al}_{30}$ [14]. Hence, we conclude that the $\text{Fe}_{70}\text{Al}_{30}$ starts already to form at 4 h of milling time and increases in intensity with milling time. This result was not evidenced from X-ray diffraction experiments (Section 3.1) because of the limit detection of this technique.

For the samples milled for 9 h and 18 h, the Mössbauer spectra were also fitted with one sextet containing two components. The first components with $\langle H_{\text{hf}} \rangle$ values equal to 32.85 T (44.20%) and 32.84 T (21.49%), respectively, are related to α -Fe. The second components with $\langle H_{\text{hf}} \rangle$ of 27.06 T (55.80%) and 26.96 T (78.51%) are also attributed to the disordered ferromagnetic bcc $\text{Fe}_{70}\text{Al}_{30}$ phase.

After 36 and 48 h of milling, no components related to α -Fe were detected in the Mössbauer spectra. Indeed, the adjustment was done with one sextet (one component) having a mean hyperfine field values of 25.72 T and 25.31 T. These values, characteristic of the disordered ferromagnetic bcc $\text{Fe}_{70}\text{Al}_{30}$ phase, are not far from those found by Hsu et al. [23] (26 T) in the case of $\text{Fe}_{70}\text{Al}_{30}$ alloy prepared by DC sputtering.

4. Conclusion

From X-ray diffraction spectra, we have followed the formation of $\text{Fe}_{70}\text{Al}_{30}$ alloy from elemental Fe and Al powder. It is found that after 27 h milling, the $\text{Fe}_{70}\text{Al}_{30}$ is formed; beyond 27 h all the Al atoms are dissolved into the α -Fe lattice leading to the formation of bcc Fe(Al) solid solution. The interpretation of Mössbauer spectra indicates that, in addition to a paramagnetic phase rich with Al which disappear after 18 h of milling, a disordered ferromagnetic $\text{Fe}_{70}\text{Al}_{30}$ starts to form at 4 h and increases in intensity with increasing milling time. After 36 h, only the disordered $\text{Fe}_{70}\text{Al}_{30}$ phase is present.

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