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Structural and hyperfine evolution of the $(Fe_{79}Mn_{21})_{1-x}Cu_x$ system under milling time

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ABSTRACT

The evolution with milling time (t_m) of the structural and hyperfine properties of mechanically alloyed $(Fe_{79}Mn_{21})_{0.85}Cu_{0.15}$ and $(Fe_{79}Mn_{21})_{0.70}Cu_{0.30}$ nominal composition samples are reported. The samples milled during t_m = 1, 3, 6, 9, 12, 15 and 18 h are characterized by X-ray diffraction (XRD) and Mössbauer spectroscopy. From the XRD results two phases are observed, a BCC one corresponding to α-Fe(Mn, Cu) and a FCC-phase associated to Fe–Mn–Cu solid solution. Mössbauer spectra show complex structure evidencing several Fe environments. Two hyperfine magnetic field distributions were used to reproduce the spectra, a high magnetic field interaction ascribed to the BCC phase and a low hyperfine magnetic field distribution linked to the FCC solid solution. An increment in the average hyperfine magnetic field (B_{hf}) and in the isomer shift (δ) values of the low hyperfine magnetic field distribution is observed when the milling time increases. All the structural and hyperfine parameters remain without changes after 9 h of milling. Once this stationary regime is archived, the B_{hf} of the $(Fe_{79}Mn_{21})_{0.85}Cu_{0.15}$ sample resulted higher than that of the $(Fe_{79}Mn_{21})_{0.70}Cu_{0.30}$ one.

1. Introduction

The FCC-Fe based system is a topic of continuous interest since these alloys display a rich and complex variety of magnetic phenomena and potential technological applications [1–3]. The renewal interest is based on fabrication routes, like ball milling, that allows to synthesizing metastable phases between immiscible elements in a nanoscopic scale [4,5]. In particular the ternary FeMnCu system belongs to this kind of attractive alloys [6,7]. Specially, the FCC-FeMn alloys have been declared as being the most adequate to describe the FCC-Fe [8] and the addition of Cu to the FeMn system has been used to stabilize the FCC-phase, showing interesting new magnetic properties. In this frame, we have focused our attention on the low Mn and Cu concentration range of the FeMnCu system [9–11].

As one of the step of this systematic research program on the magnetic and structural properties of the of $(Fe_{79}Mn_{21})_{1-x}Cu_x$ $(0.00 \leq x \leq 0.30)$ system, we present here a study of the influence of the milling time on the evolution of the formed phases of $(Fe_{79}Mn_{21})_{0.85}Cu_{0.15}$ and $(Fe_{79}Mn_{21})_{0.70}Cu_{0.30}$ samples using X-ray diffraction and Mössbauer spectroscopy.

2. Experimental

Alloys of $(Fe_{79}Mn_{21})_{0.85}Cu_{0.15}$ and $(Fe_{79}Mn_{21})_{0.70}Cu_{0.30}$ nominal composition were prepared by milling the pure elements in a vibratory horizontal mill (f = 33 Hz, Ar atmosphere, steel vials and ball; and ball to sample mass ratio equal to 20:1). Both samples were milled during different total times (t_m = 1, 3, 6, 9, 12, 15 and 18 h), with stops of 15 min each 45 min.

The resulting powdered alloys were characterized by X-ray diffraction (XRD) with a Philips PW1710 diffractometer (Cu-Kα radiation), in the Bragg-Brentano geometry, with a step mode collection of 0.02°, 1 s by step, with 2θ ranging from 20° to 100°.

Mössbauer spectra (MS) were taken in transmission geometry using a 5mCi ^{57}Co*Rh* source and recorded in a standard constant acceleration spectrometer in two different velocity ranges: [−4, 4 mm/s] and [−8, 8 mm/s]. Due to the existence of different iron environments in the samples, the MS were analyzed using a large number (40) of subspectra separated by regular magnetic hyperfine field intervals (hyperfine field distributions) with non-zero probability at zero hyperfine fields. Linear correlation between isomer shifts (δ) and hyperfine magnetic field (B_{hf}) as well as between quadrupole shift (ε) and B_{hf} were allowed [12]. Isomer shift values are referred to α-Fe at 300 K.

3. Results and discussion

Diffraction lines of BCC and FCC structures are observed in the XRD patterns shown in Fig. 1. For t_m = 1 h, the BCC structure is the main detected phase for both studied concentrations, while when the t_m increases the BCC structure almost vanishes for x = 0.15 sample and completely disappears for the x = 0.30 one. At milling times higher than 9 h, the patterns of both samples remain with-

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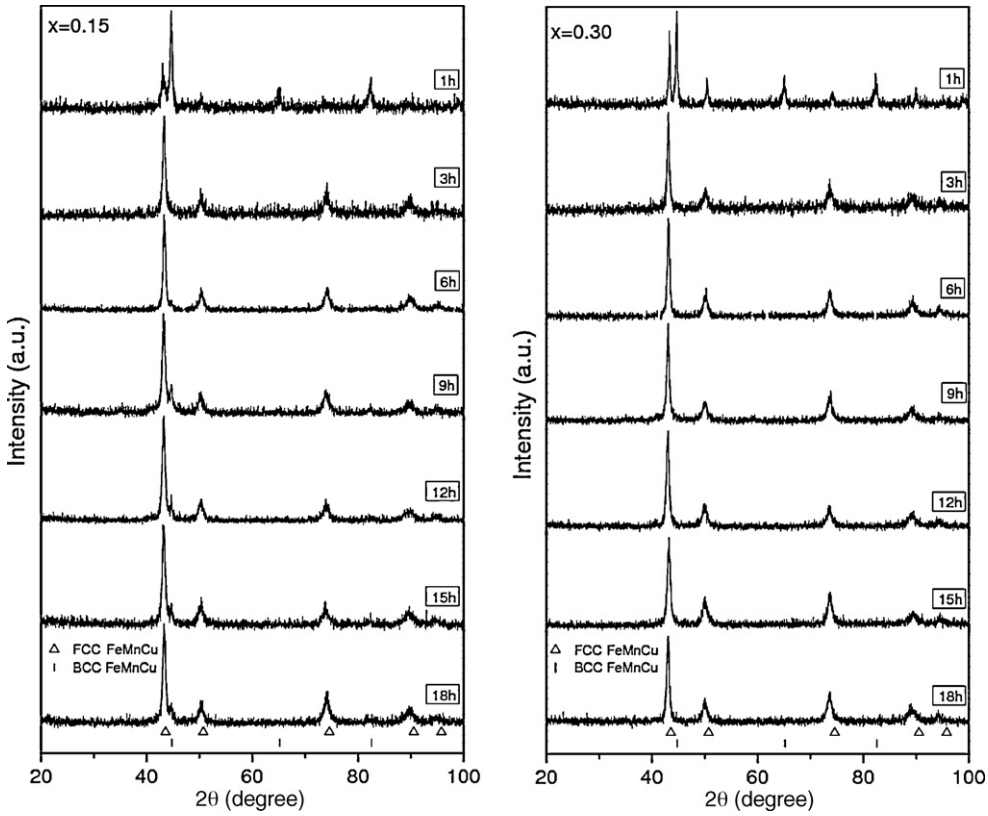

Fig. 1. X-ray diffractograms labeled with milling time. On the left $x = 0.15$ and on the right $x = 0.30$ samples.

out changes. These results strongly suggest that the increase of milling time help to the formation of a FCC solid solution, stabilized by the Cu addition given that the BCC lines are absent in the $x = 0.30$ patterns. The average crystallite sizes, determined using the Scherrer approximation [13] and considering the most intense peak of each phase, resulted of the order of 10 nm for both phases. The lattice parameter of the FCC-phase increases with the milling time. The magnitude of the increment in relation to the expected values for $Fe_{79}Mn_{21}$ [14] is approximately 0.65% and 1.05% for $x = 0.15$ and $x = 0.30$ samples, respectively. The observed lattice expansion is attributable to the formation of a ternary solid solution and to the strain introduced during the milling process and to the magneto-volume effects. These last facts were endorsed by other authors on mechanically alloyed samples [6,15].

The low velocity range Mössbauer spectra for different milling times are displayed in Fig. 2. They were reproduced with two hyperfine magnetic field distributions (HMFD), one of high field ($B_{hf} = 31$ T and $\delta = 0.00$ mm/s) and other of low field. This choice is based on the results of the different tested fitting models. It was firstly proposed two quadrupolar electric interactions, however the spectra were not well reproduced, particularly the broadening in the bottom part of the signal. Then, the central part of the present set of spectra was fitted with a hyperfine magnetic low field distribution, which includes a non-vanishing probability at zero fields to take into account the small grain size effect on the magnetic behavior like superparamagnetism or blocking effects, probable concentration inhomogeneties, and paramagnetic components. It is worth to mention that attempts to also include a single line as in Ref. [16] do not noticeably improve the fits. Then, the simplest model, *i.e.*, a HMFD with non-vanishing probability at zero field, was adopted to reproduce the present set of spectra. Supported by the XRD results and those reported in [4,17], the high field distribution is ascribed to the BCC-Fe (Mn, Cu) solid solution and the low field interaction to a FCC-FeMnCu solid solution.

After $t_m = 1$ h of milling, the spectra corresponding to both samples are dominated by the broad sextet associated to the BCC-solid solution, being the relative fractions 88% and 74% for $x = 0.15$ and 0.30 samples, respectively. For higher milling times, the amount of this phase strongly decreases reaching a relative fraction of 15% for $x = 0.15$ and becoming not noticeable in the $x = 0.30$ sample. For $x = 0.15$ and longer milling times, the relative fraction of the BCC phase remains constant in agreement with XRD results.

The low HMFD probabilities are shown in Fig. 3. There, it is noticed that for milling times shorter than 9 h, a high contribution at low field (closer to zero) is observed while the maximum of the probability distribution shifts to higher values as milling time increases. The B_{hf} average hyperfine magnetic field and the δ isomer shift values (Fig. 4) of both samples slightly increases when the milling process proceeds, presenting a two stage behavior, one for $t_m < 9$ h and other for $t_m > 9$ h, suggesting composition inhomegenities in the FCC solid solution at low milling times.

The Néel temperature of the FCC-FeMn phase is Mn content dependent [18], being lower than RT for Mn concentrations smaller than 14 at.%, base in this fact a fraction of the alloy could be paramagnetic at RT. Regarding that, it is tempting to associate the contribution at zero fields observed in Fig. 3 to this paramagnetic phase and/or to stacking faults [16]. During the last stage of milling ($t_m > 9$ h), the hyperfine parameters remain without changes indicating that the chemical mixing of the elements was reached. Finally, it is also noticed (see Fig. 4) that B_{hf} and δ values depend on Cu content, *i.e.*, as Cu content increases B_{hf} decreases and δ increases for $t_m > 9$ h, similar to previous results reported on Fe–Cu samples

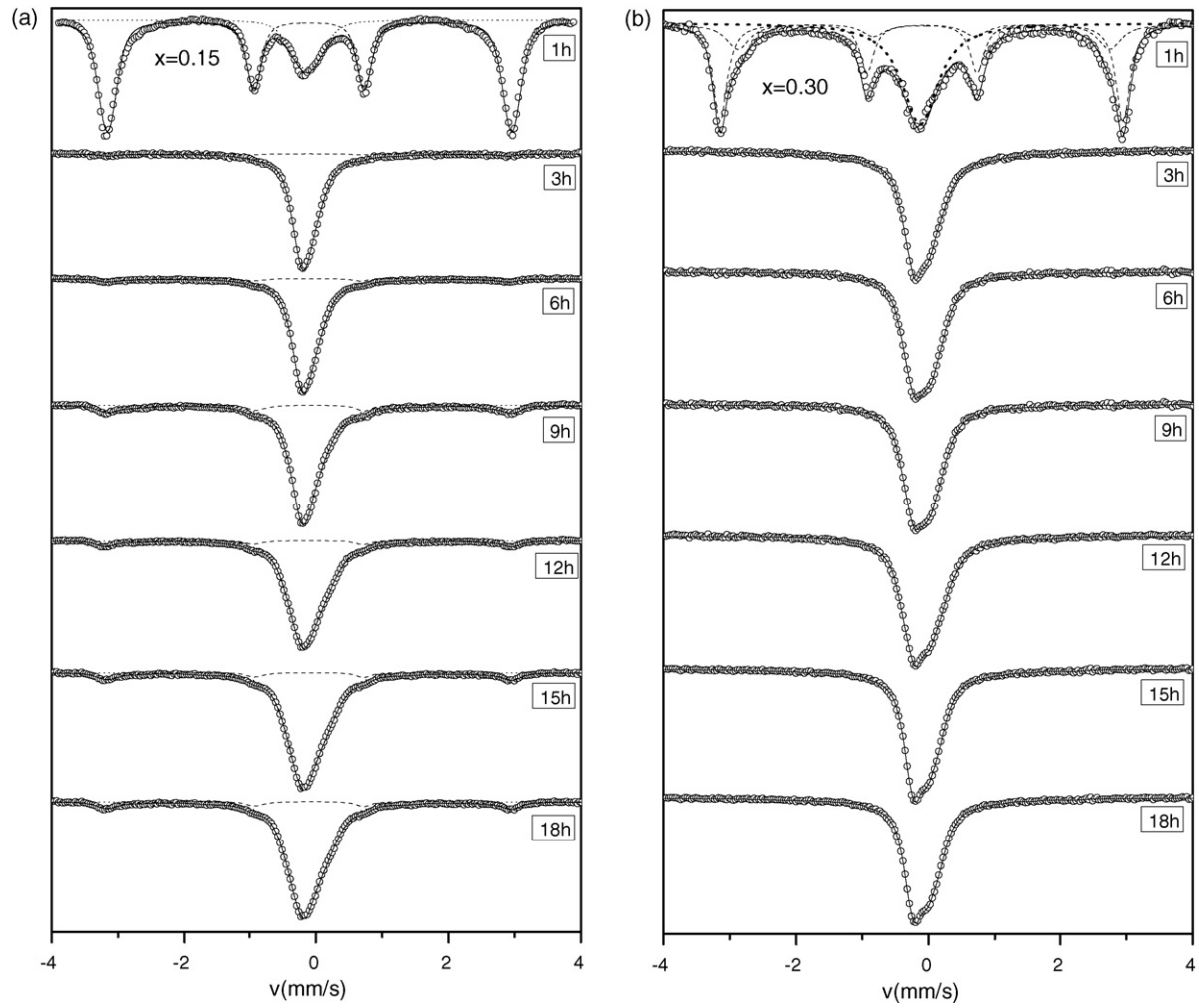

Fig. 2. Mössbauer spectra labeled with the milling time. On the left $x = 0.15$ and on the right $x = 0.30$ samples, respectively. (a) Dash line: high field distribution interaction and (b) dot line: low field distribution interaction.

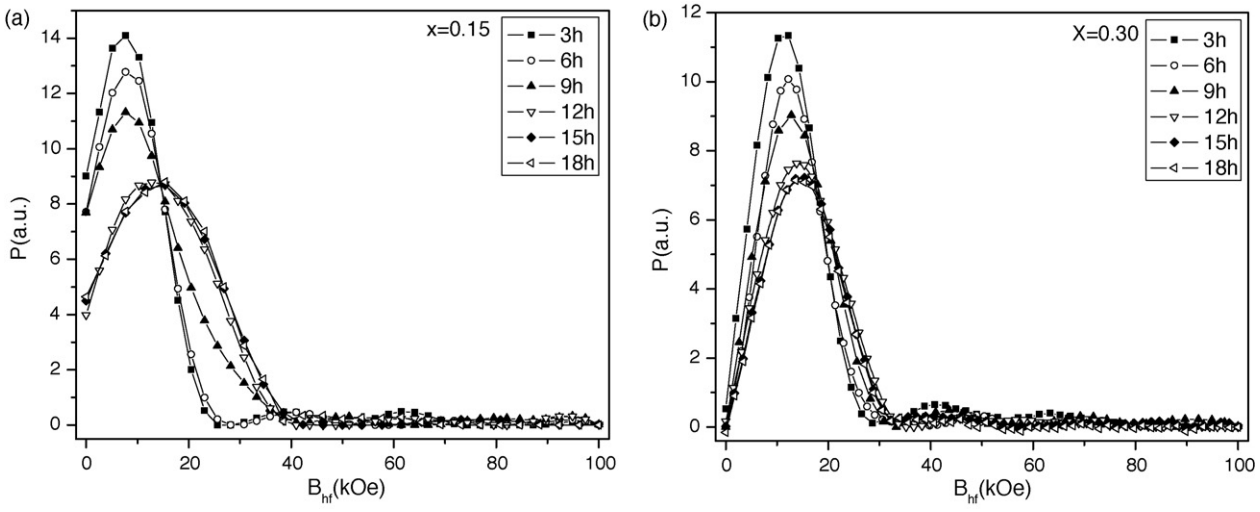

Fig. 3. Low field hyperfine magnetic distributions. On the left $x = 0.15$ and on the right $x = 0.30$.

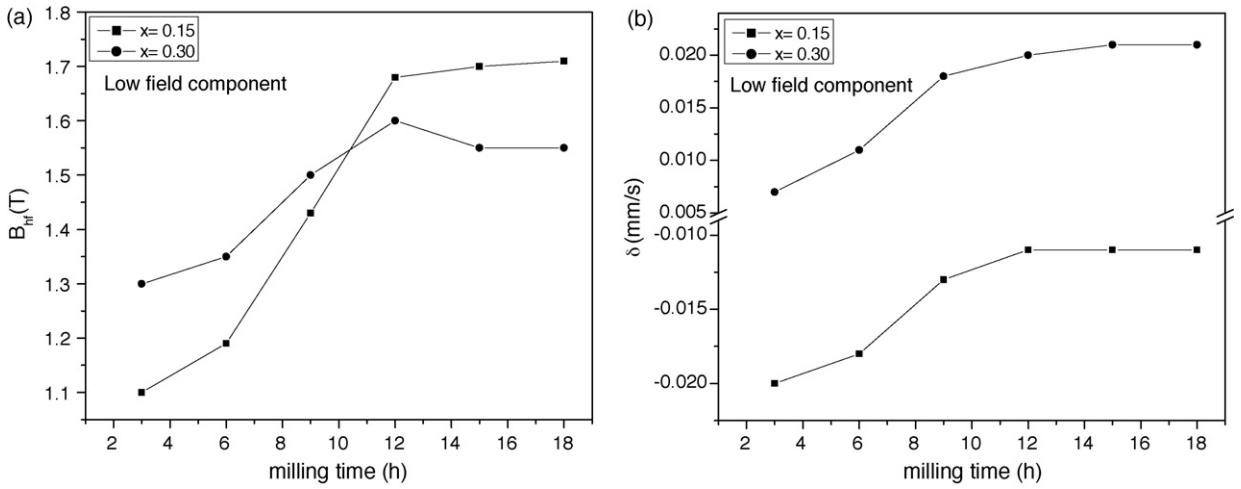

Fig. 4. Evolution with milling time of the average hyperfine field (B_{hf}) and isomer shift (δ) values for the low field component.

[19]. Both facts strongly suggest the formation of a FCC-FeMnCu solid solution.

4. Conclusions

The influence of the milling time on the phase formation of $(Fe_{79}Mn_{21})_{0.85}Cu_{0.15}$ and $(Fe_{79}Mn_{21})_{0.70}Cu_{0.30}$ systems were studied using Mössbauer spectroscopy and X-ray diffraction. The progressive formation of a FCC-FeMnCu solid solution is observed from evolution with milling time of the XRD patterns and the Mössbauer hyperfine parameters. It was observed that the milling process occurs in two steps, the structural and hyperfine parameters reach approximately constant values for milling times longer than 9 h. The evolution of the FCC hyperfine parameters with milling time suggests the presence of composition fluctuations in the alloys in the first step of milling and the formation of a homogenous solid solution in the second one.

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