

## Magnetic properties of ball-milled $\text{Fe}_{0.6}\text{Mn}_{0.1}\text{Al}_{0.3}$ alloys

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### Abstract

The FeMnAl-disordered alloy system exhibits, depending on the composition and the temperature, a rich variety of magnetic phases including the occurrence of ferromagnetism, antiferromagnetism, paramagnetism and spin-glass and reentrant spin glass behaviors. These latter phases result from the presence of atomic disorder and magnetic dilution and from the competing exchange interactions taking place between an Fe atom and its Mn and Fe first neighbors. The use of mechanical alloying in order to prepare these alloys is specially interesting since it allows to introduce in a progressive way large amounts of disorder. In this work, we describe the evolution with the milling time of the temperature dependence of the magnetic properties of mechanically alloyed  $\text{Fe}_{0.6}\text{Mn}_{0.1}\text{Al}_{0.3}$  samples. The materials were prepared in a planetary ball mill using a balls-to-powder mass ratio of 15:1 and pure (99.95 at%) Fe, Mn and Al powders for times up to 19 h. The X-rays diffraction (XRD) spectra show the coexistence of three phases at short milling times. For milling times over 6 h, only the FeMnAl ternary alloy BCC phase is observed. Mössbauer spectroscopy reveals the complete formation of the FeMnAl alloy after 9 h milling time. The magnetic characterization showed that all the samples were ferromagnetic at room temperature with coercivities decreasing from 105 Oe (3 h milled sample) down to 5 Oe in the case of the sample milled for 19 h.

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### 1. Introduction

Mechanical alloying (MA) based on high-energy ball milling is a simple technique, based on solid-state reaction and atomic diffusion, to produce nonequilibrium powdered materials which, in some cases, cannot be obtained by conventional melting. The synthesis of numerous binary alloys was achieved by means of mechanical alloying from elemental powders, leading to nanocrystalline or amorphous powders. Examples of binary alloys prepared by mechanical alloying are the Fe–Al system [1], as well as the Fe–Mn one [2] where the structural, microstructural and magnetic properties were studied as a function of alloying time. In contrast, only a few studies of the ternary

Fe–Mn–Al system by mechanical alloying process have been reported in the literature [3–6]. These studies cover the alloys series  $\text{Fe}_x\text{Mn}_{0.7-x}\text{Al}_{0.3}$  ( $0.4 \leq x \leq 0.7$ ),  $\text{Fe}_x\text{Mn}_{0.8-x}\text{Al}_{0.2}$  ( $0.5 \leq x \leq 0.8$ ) and  $\text{Fe}_x\text{Mn}_{0.1}\text{Al}_{0.9-x}$  ( $0.1 \leq x \leq 0.4$ ), and describe the effects of varying the Mn (or Al) concentration on the structural characteristics (crystalline structure and lattice parameter) as well as on the grain size. In general, the magnetic and structural properties of these systems are very similar to those exhibited by powders of melted alloys with the same composition, especially when they are mechanically alloyed for long times. Interest in this system comes from the fact that it exhibits good oxidation/corrosion resistance and a range of different magnetic phases, including ferromagnetic and antiferromagnetic, as well as pure and reentrant spin-glass (SG and RSG) phases. In this work, we will study the alloy  $\text{Fe}_{0.6}\text{Mn}_{0.1}\text{Al}_{0.3}$  which can present a soft magnetic

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behavior and has been reported to behave as a RSG phase at low temperature.

## 2. Experimental procedure

Elemental Fe, Mn and Al powders with a purity better than 99.95% were mixed stoichiometrically to obtain a nominal composition of  $\text{Fe}_{0.6}\text{Mn}_{0.1}\text{Al}_{0.3}$ . The powders were introduced in four jars of template Cr steel with balls of the same material. Ball mass-to-powder mass (BM/PM) ratio of 15:1 was selected to produce the alloyed powders. The jars were sealed and evacuated to approximately  $5 \times 10^{-2}$  mbar and positioned in a planetary ball mill (Pulverisette 5). To avoid overheating, cycles of 1 h milling and 1 h rest were performed. The milling process was carried out using a speed of 280 rpm and milling times of 3, 6, 9, 12, 15 and 19 h. Mössbauer spectra (MS) were performed using transmission geometry with a  $\text{Co}^{57}$  source and fitted with the MOSFIT program [7], using  $\alpha\text{-Fe}$  as reference. X-ray diffraction (XRD) has been obtained with  $\text{Cu } K_{\alpha}$  radiation. The hysteresis loops were measured with a conventional VSM with a maximum field of 2 T.

## 3. Experimental results and discussion

Fig. 1 shows the XRD patterns of all the prepared samples. It can be noted that the sequence of the diffraction lines corresponds to a typical BCC structure. However, a zoom of the principal peak, the one observed at  $2\theta$  between  $40^{\circ}$  and  $49^{\circ}$ , for the sample milled during 3 h (shown in Fig. 2) reveals some peak inner structure. In fact, it can be deconvoluted into three peaks, which are attributed to the  $\alpha\text{-Mn}$  ( $43.2^{\circ}$ ), the ternary Fe–Mn–Al BCC alloy ( $44.1^{\circ}$ ) and  $\alpha\text{-Fe}$  or  $\alpha\text{-Al}$  ( $44.7^{\circ}$ ). In this figure, it can also be seen that for milling times over 6 h, the peak corresponding to the ternary alloy is the largest one, becoming unique for milling times over 12 h. By fitting the peak of the ternary alloy to a Lorentzian function and using its width and position, the variation of the mean grain size and lattice parameter as a function of the milling time were determined. The grain size remains nearly constant at a value of 16 nm, while the lattice parameter grows from 2.910 to 2.914 Å for the longer milling time. These lattice parameters are in good agreement with previous reports for alloys with this composition produced by melting [8] and long-milling time mechanical alloying [5].

Fig. 3 shows the MS of some of the samples and their corresponding hyperfine field distributions (HFD). The MS of the sample milled for 3 h was fitted with a broad singlet, a doublet and an HFD. This type of fit was also considered for powders of the  $\text{Fe}_{0.60}\text{Mn}_{0.15}\text{Al}_{0.25}$  melted alloy [8], where the singlet and the doublet correspond to Fe paramagnetic sites on the ternary BCC FeMnAl disordered alloy surrounded by symmetric and asymmetric charge distribution, respectively. The HFD corresponds to those Fe sites with a largest number of Fe nearest neighbors (nn). In this HFD, it can be noted that the most probable site is

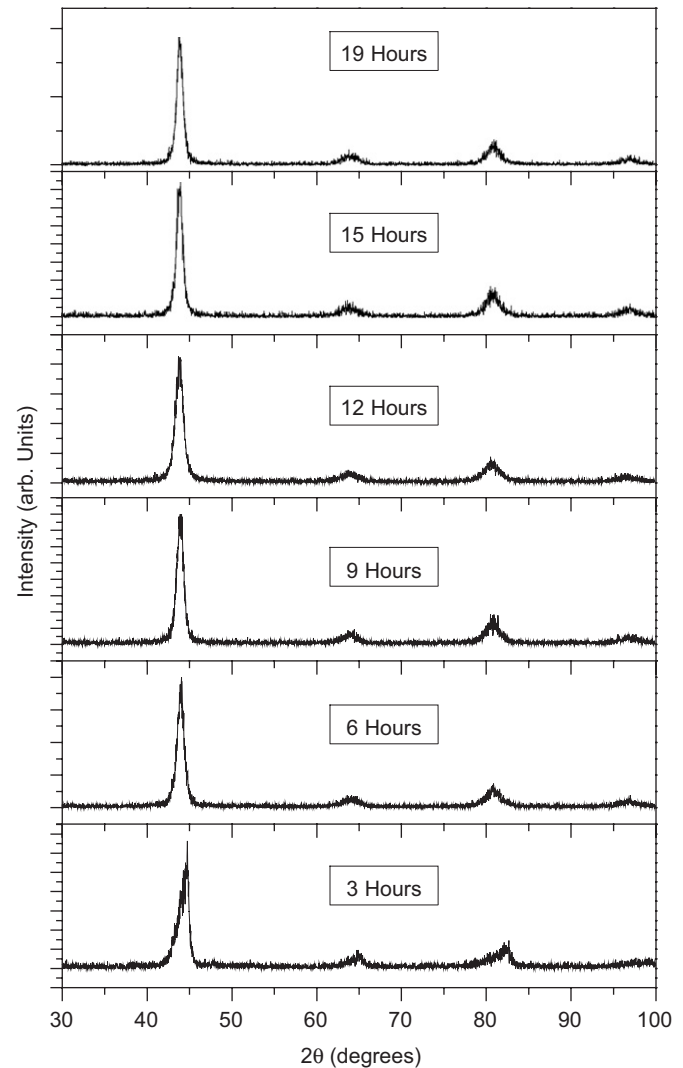


Fig. 1. XRD spectra of the prepared samples.

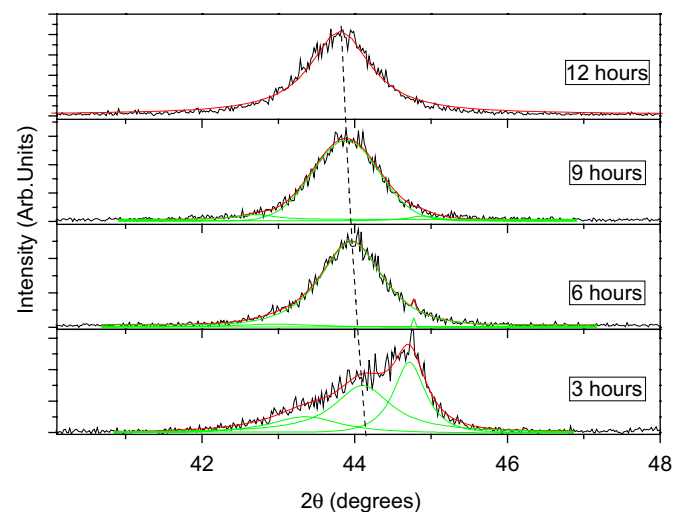


Fig. 2. Detail of the main diffraction peak for different samples. The best fit of the peak to Lorentzian functions is shown. A dashed line is included to indicate the change in lattice parameter.

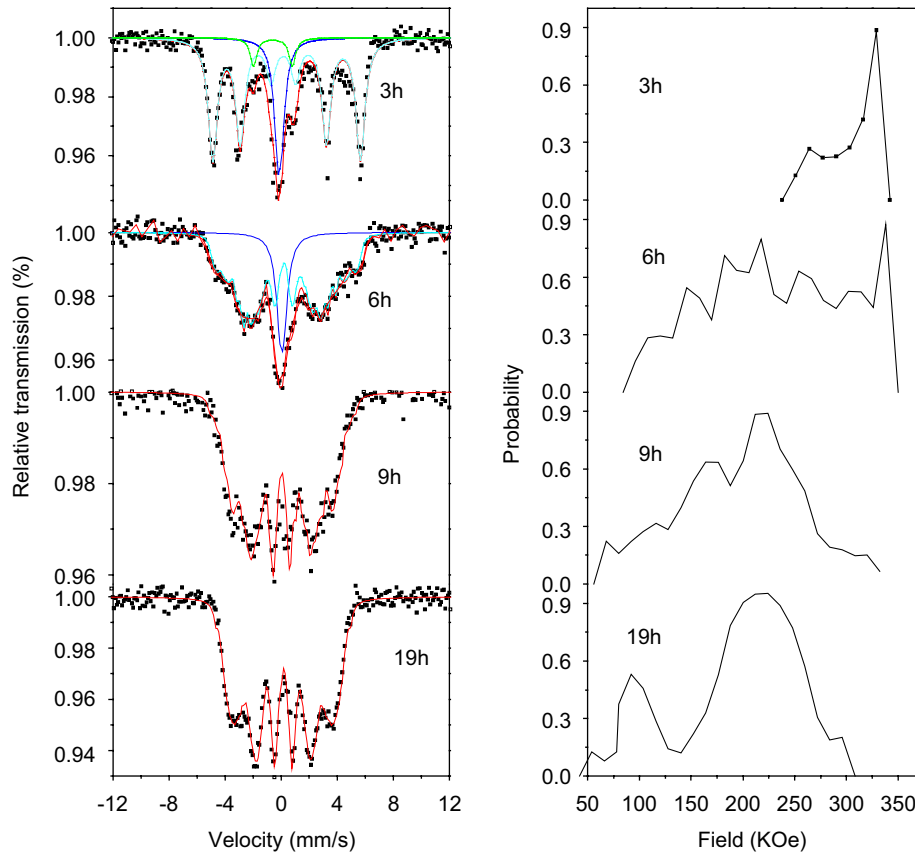


Fig. 3. Mössbauer spectra of the prepared samples. The fitting curves and the respective hyperfine fields are also shown.

that of pure iron with a field of 330 kOe and another site appears at nearly 262 kOe, which can be attributed to an Fe site with two Mn or two Al or one Mn and one Al as nn [8]. The sample milled for 6 h was fitted with a singlet and a broad HFD showing now that the charge distribution around the paramagnetic Fe sites is symmetric and that the ferromagnetic Fe sites are more distributed. The different peaks observed in the HFD show that now we have pure Fe sites (330 kOe peaks) and sites with one, two or more Mn or Al atoms as nn. The spectra obtained for 9 and 19 h milling are also shown in Fig. 3. These spectra were fitted considering a HFD exclusively. The spectra obtained for 12 and 15 h and their corresponding HFD are very similar to those obtained for the 19 h sample.

Fig. 4 shows the variation of the obtained mean hyperfine field (MHF) with the milling time. It can be noted that the MHF decreases from 312 kOe for the 3 h milled sample down to 188 kOe for the 9 h milled one and then it remains nearly constant. The decrease is due to the diffusion of the Mn and Al atoms inside the Fe lattice. This decrease ends when the alloy is homogenized. XRD results showed that the alloy is the predominant phase after 6 h milling, but according to the Mössbauer results, the alloy local composition continues to vary up to 19 h milling time, when the Mn and Al distribution is homogenized.

The hysteresis loops measured in all the samples show a typical behavior of a ferromagnetic sample with a

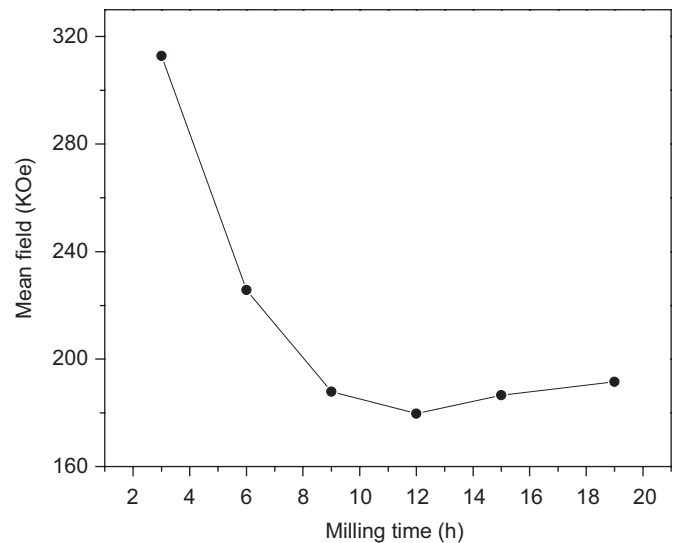


Fig. 4. Variation of the mean hyperfine field on the different samples, as obtained from the fitting of Mössbauer spectra.

saturation field near 2 T and a saturation magnetization of about 120 emu/g. The variation of the coercive force with the milling time is shown in Fig. 5. We can note that the coercivity decreases from 105 Oe for the 3 h milled sample down to 5 Oe for the 19 h milled one.

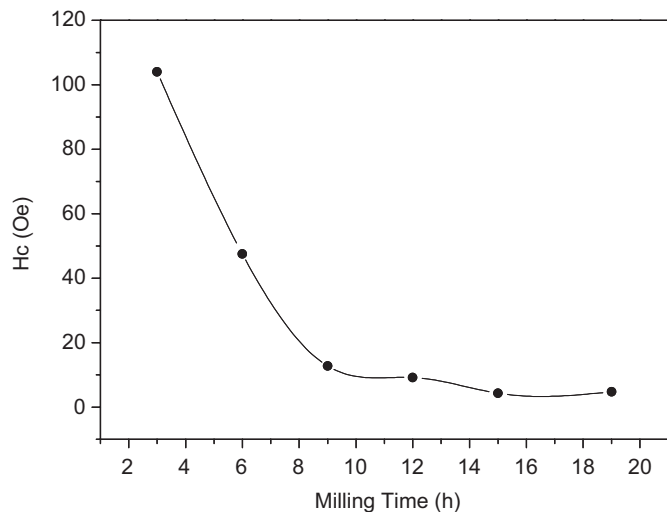


Fig. 5. Evolution of the coercitive field with the milling time.

#### 4. Conclusions

From the results of this work, we can conclude that the  $\text{Fe}_{0.6}\text{Mn}_{0.1}\text{Al}_{0.3}$  samples produced by mechanical alloying present a ferromagnetic character for the different milling times used. They are soft magnetic samples, improving this character with the increase of the milling time. After 6 h milling the BCC, disordered alloy is the main phase of the system, but the local degree of disorder continues to evolve

up to 19 h milling time as revealed by the evolution of the HFD.

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