

Characterization of the $\text{Fe}_{90-x}\text{Si}_{10}\text{Cr}_x$ ($x=10, 15$) nanostructured powders prepared by mechanical alloying

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Received: 30 Jan 2012, revised: 29 Mars 2012, accepted: 05 April 2012

Abstract

In this study, structural and magnetic properties of nanocrystalline $\text{Fe}_{80}\text{Si}_{10}\text{Cr}_{10}$ and $\text{Fe}_{75}\text{Si}_{10}\text{Cr}_{15}$ powders produced by mechanical alloying (MA) have been investigated and examined by X-ray diffraction and ^{57}Fe Mössbauer spectrometry. Mechanical alloying was carried out in a planetary high energy ball mill starting from pure elements of iron, silicon and chrome. After 15 h of milling, it is observed the formation of two bcc solid solutions $\alpha\text{-Fe}_1$ (Si, Cr) and $\alpha\text{-Fe}_2$ (Si, Cr) for the $\text{Fe}_{80}\text{Si}_{10}\text{Cr}_{10}$ alloy. Their grain sizes decrease with milling time and attains 23 nm and 11 nm respectively. For the $\text{Fe}_{75}\text{Si}_{10}\text{Cr}_{15}$ alloy the XRD shows the formation of the bcc and the cfc solid solution with a low concentration. The lattice parameter of the bcc solid solution increases with increasing time and chrome content. Mössbauer spectrum at room temperature of the $\text{Fe}_{80}\text{Si}_{10}\text{Cr}_{10}$ alloy resulted in the formation of two contributions, ferromagnetic and paramagnetic with a low concentration of 4 %. Addition of Cr as in the case $\text{Fe}_{75}\text{Si}_{10}\text{Cr}_{15}$ alloy increases the paramagnetic contribution with a relative concentration of 17.5 %.

Key-words: Nanocrystalline materials, Mechanical alloying, FeCrSi alloy, X-ray diffraction, ^{57}Fe Mössbauer spectrometry.

PACS:75. 50.Tt; 87. 20.Ev; 61. 10.Nz; 76.80+y.

1. Introduction

The nanostructured powders or particles with very fine crystalline grains can be synthesized by different techniques. In particular, the influence of nanometer grains on the structural and magnetic properties of these materials is intensively studied [1-3]. The mechanical alloying or high energy ball milling can be used conveniently to prepare nanostructured materials with often improved mechanical and magnetic properties [4]. The basic mechanism in milling elemental or prealloyed powders consists in a succession of fracture and welding that favors the formation of particles composed of nanometric grain size. The FeSiCr alloys have been subject of several studies related with their structural and magnetic properties [5, 6].

Addition of Si to Fe alloys enhances the electrical resistivity and therefore reduces the Eddy currents. And the addition of Cr in Fe-based alloys increases mechanical strength as well as oxidation and corrosion resistance at atmospheric and higher temperatures. Also, its magnetism under nanometer structure has been scarcely reported. It is interesting to examine the crystal structure and its corresponding magnetism as the mean grain size reduced down to a nanometer scale in the purpose of improving the magnetic properties of materials.

In this paper, the effect of milling time on the microstructure and magnetic properties were investigated for the nanocrystalline $\text{Fe}_{80}\text{Si}_{10}\text{Cr}_{10}$ and the $\text{Fe}_{75}\text{Si}_{10}\text{Cr}_{15}$ alloys prepared by mechanical alloying.

2. Experimental procedure

Mechanical alloying of the $\text{Fe}_{80}\text{Si}_{10}\text{Cr}_{10}$ and the $\text{Fe}_{75}\text{Si}_{10}\text{Cr}_{15}$ powders were carried out in a planetary high energy ball mill (Fritsch Pulverisette P7) starting from pure elements of iron,

silicon and chromium, with different concentration. In all, mechanical milling was carried out at 400 rpm under argon atmosphere, using hardened steel balls and vials. The ball to powder weight ratio was 17:1. The milling times were: 5, 10 and 15 h. Structural changes were studied by X-ray diffraction (XRD) in a Philips diffractometer using $\text{CoK}\alpha$ radiation ($\lambda_{\text{Co}} = 0.1788$ nm). The structural and microstructural characteristics: lattice parameters, grain size and microstrains, were derived from the refinement of X-ray patterns using Maud program [7] based on the Rietveld method [8]. The ^{57}Fe Mössbauer spectra were performed at room temperature in a transmission geometry using a conventional constant acceleration spectrometer and fitted using the MOSFIT program [9]. All the isomer shifts were measured relative to α -iron at room temperature and α -iron was also used for calibration. The hyperfine parameters for these alloys were found by fitting the Mössbauer spectra.

3. Results and discussions

3.1 X-ray diffractions

Fig. 1. displays the XRD of the $\text{Fe}_{75}\text{Si}_{10}\text{Cr}_{15}$ powder as function of milling time. The best refinement of X-ray diffraction patterns of the powders is obtained with the isotropic model with full profiles of the diffraction peaks given by isotropic grain shape. The broadening of the diffraction peaks and the decrease in their heights with increasing milling time are due to the crystallite size refinement down to the nanometer scale and the increase of the internal strain. After 5 h of milling time, we

observed the formation of a disordered solid solution type bcc. At 10 h of milling, a disordered solid solution type cfc structure appears, this phase is clearly observed after 15 h of milling time a relative lower concentration of about to 12 %. Comparable results with the

presence of α -Fe (Si, Cr) and γ -Fe (Si, Cr) phases were also obtained in the ternary FeCrCo [10] and also in the binary FeCu [11].

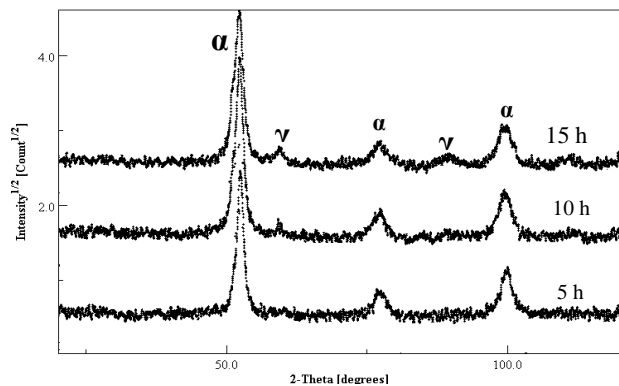


Fig. 1. XRD patterns of the Fe₇₅Si₁₀Cr₁₅ powders milled for various times.

Fig. 2. shown the variation of lattice parameter of phase α -Fe (Si, Cr) of the Fe₇₅Si₁₀Cr₁₅ powder during milling time. It is found that the lattice parameter varies little up to 5 h of milling. For milling times longer, there is an increase almost linearly with milling time. This increase may be related to the predominant distribution of chromium atoms (in higher concentration) in the solid solution α -Fe (Si, Cr) knowing that the atomic radius of chromium ($R_{Cr} = 0.185$ nm) is higher than that of iron ($R_{Fe} = 0.123$ nm) [12].

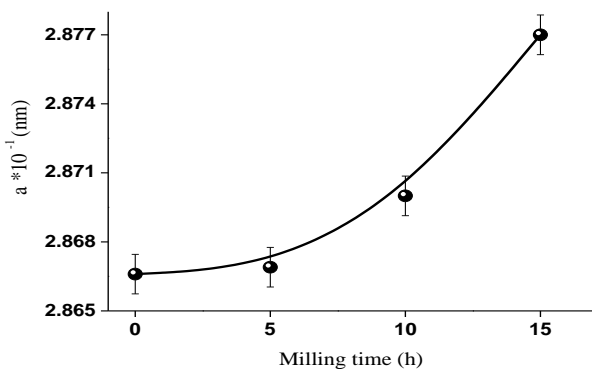


Fig. 2. Evolution of lattice parameters of the α -Fe (Si, Cr) solid solution of the Fe₇₅Si₁₀Cr₁₅ powder with milling time.

Fig. 3. show the Rietveld refinement of the XRD pattern of the ball-milled Fe₈₀Si₁₀Cr₁₀ powder mixture for 15 h. It is observed that the best fit of the diffractograms X Rietveld method is obtained using two disordered solid solutions: α 1-Fe (Si, Cr) and α 2-Fe (Si, Cr)-type bcc, with an average concentration on 90 % and 10 % respectively. The existence of the two bcc Fe structure can be assigned to the non-homogeneity in concentration of the milled Fe₈₀Si₁₀Cr₁₀ powder mixture leading the different diffusion process of Si and Cr

into the bcc Fe matrix induced by high energy ball milling. This effect does originate two types of atomic environments of Fe with different lattice parameters or/and grain size.

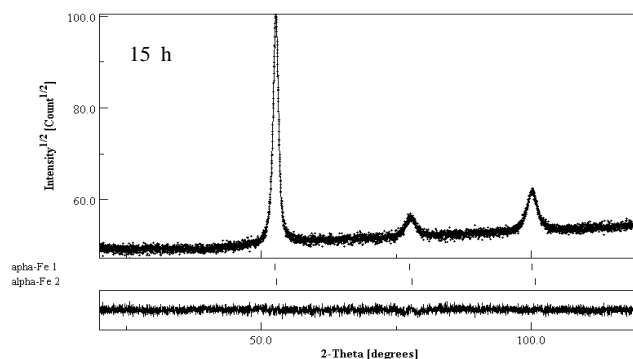


Fig. 3. Rietveld refinement of the XRD pattern of the ball-milled Fe₈₀Si₁₀Cr₁₀ powder mixture for 15 h.

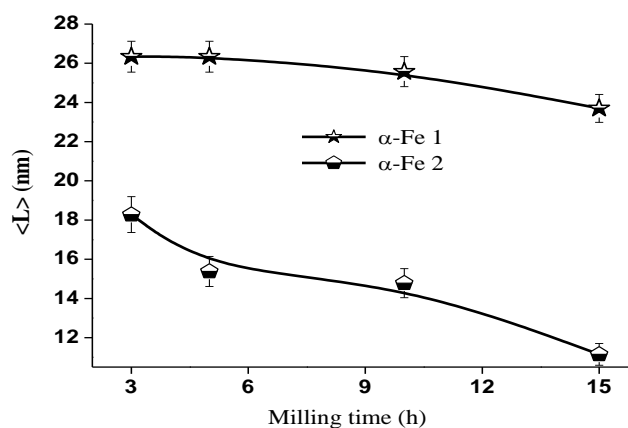


Fig. 4. Milling time dependence of the mean crystallite size for α -Fe 1 and α 1-Fe 2 structures of the Fe₈₀Si₁₀Cr₁₀ powder.

Since the two bcc α -Fe structures have the different average crystallite $\langle L \rangle$, Fig. 4. illustrated the variation of the crystallite size of the two solid solution with milling time. The crystallite size of both structures decrease to 23 and 11 nm respectively, after 15 h of milling. A similar result has been proposed in the nanostructured Fe₉₂P₈ alloy [13, 14] and in the FeCoAl alloy [15].

3.2 Mössbauer spectrometry analysis

The The Mössbauer spectra of Fe₈₀Si₁₀Cr₁₀ and Fe₇₅Si₁₀Cr₁₅ powders, taken at room temperature, for the 15 h of milling time and their hyperfine field distribution curves correspond are shown in Fig. 5. It is observed the spectrum of the Fe₈₀Si₁₀Cr₁₀ powder consists of sextet with broad lines characteristic of a disordered structure where iron atoms are largely replaced by atoms of silicon and/or chromium atoms and a singlet with a relative concentration of about 4 % correspond of paramagnetic phase. In the case of Fe₇₅Si₁₀Cr₁₅ powder, the Mössbauer spectrums have also composed of two contributions: one is ferromagnetic phase, consisting of sextet with broad lines due to the substitution of silicon and chromium, the second is a singlet paramagnetic phase with a relative concentration of 17.5%.

The hyperfine distributions $P(B_{hf})$ of the Fe₈₀Si₁₀Cr₁₀ can be unambiguously separate in tow regions: one with low fields and probabilities (< 20 T, H_2 (probable) = 17 T) and the other with high fields and probabilities (range 20-33 T, H_1 (probable) = 27 T), with a relative area ratio of 9 and 91%, respectively. This result is reported in detail in reference [16]. But the hyperfine field distribution curve $P(B_{hf})$ of the Fe₇₅Si₁₀Cr₁₅ powder milled for 15 h (Fig.5 .b) can be in fact, fitted with 4

Gaussians components, corresponding to 4 different domains, with values of magnetic fields. $B_1 = 17$ T can be a chromium-rich FeCr environment where iron atoms may have 5-7 chromium atoms on the two first coordination sphere, the value of B is comparable to that found in the ternary system FeCrCo and identical to that obtained in the binary FeCr [10]. $B_2 = 22$ T can be an environment (Fe, Si, Cr) rich in chromium and silicon.

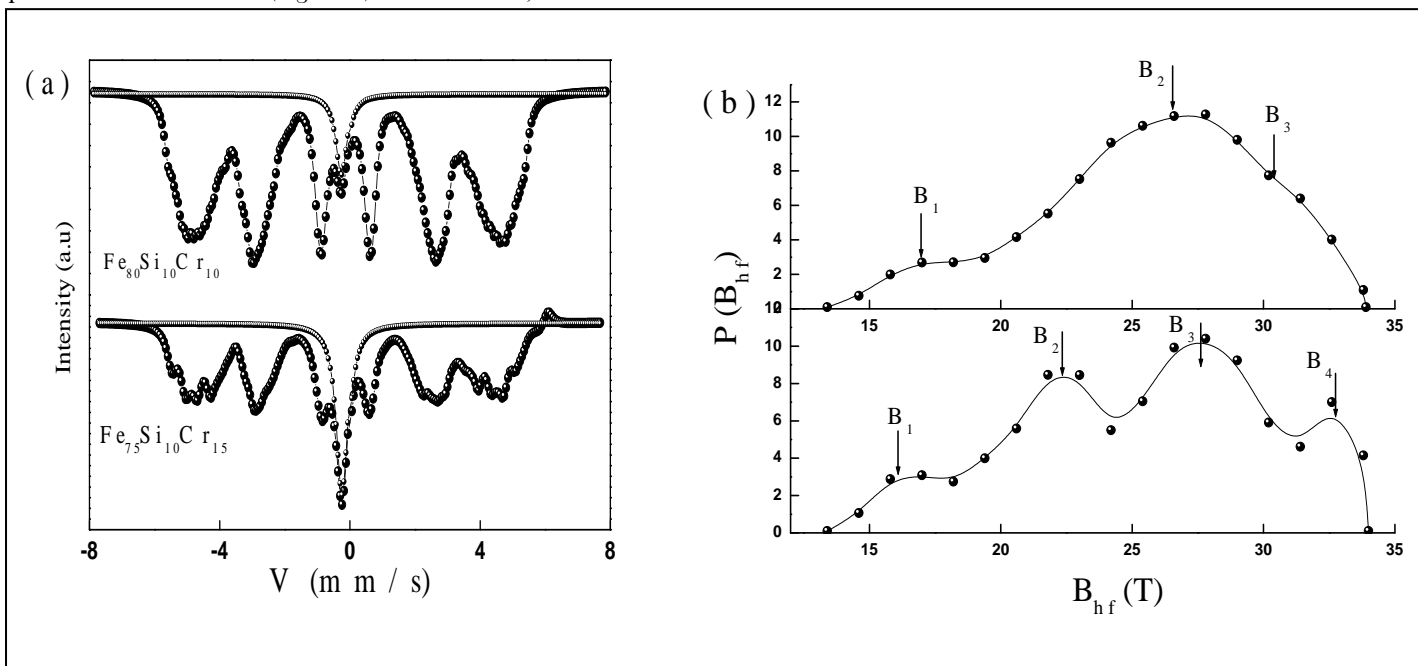


Fig. 5. Mössbauer spectra and the corresponding hyperfine field distribution Fe₈₀Si₁₀Cr₁₀ and the Fe₇₅Si₁₀Cr₁₅ powders milled 15 h.

$B_3 = 28$ T can be an environment (Fe, Si, Cr) rich in iron, where iron atoms are surrounded by two chromium atoms on the first two coordinations, or one atom of chromium and a silicon atom. $B_4 = 32.7$ T is probably an environment similar to that of pure iron which had is not alloyed with Si and Cr, with a relative fraction is 10 %.

Table 1.

Hyperfine parameters of the Fe₈₀Si₁₀Cr₁₀ and the Fe₇₅Si₁₀Cr₁₅ powders milled for 15 h.

Sample	Ferromagnetic phase		Paramagnetic phase	
	IS (mm/s)	$\langle B \rangle$ (T)	IS (mm/s)	%
Fe ₈₀ Si ₁₀ Cr ₁₀	0,05	26,5	-0,09	4
Fe ₇₅ Si ₁₀ Cr ₁₅	-0,02	22,5	-0,07	17,5

The hyperfine parameters deduced from the fitting of the Mössbauer spectra of the milled of the Fe₈₀Si₁₀Cr₁₀ and the Fe₇₅Si₁₀Cr₁₅ powders mixture for 15 h are summarized in [Table1](#).

It can be inferred that the paramagnetic component appears in mixtures Fe₈₀Si₁₀Cr₁₀ and Fe₇₅Si₁₀Cr₁₅ powders increasing the chromium content. It is therefore possible that this phase is largely composed of Cr atoms substituted for iron.

4. Conclusion

The nanocrystalline alloys Fe₈₀Si₁₀Cr₁₀ and Fe₇₅Si₁₀Cr₁₅ were prepared by high energy milling. The formation of these alloys has been followed by X-ray diffraction and Mössbauer spectroscopy.

In the case of the powder mixture of composition Fe₈₀Si₁₀Cr₁₀, the X-ray diffraction shows the formation of two solid solutions $\alpha 1$ -Fe (Si, Cr) and $\alpha 2$ -Fe (Si, Cr) after 15 h. Mössbauer spectra identify two magnetic components. The first is ferromagnetic and can be associated with the formation of two disordered solid solutions. As the second one, a paramagnetic type has a low relative concentration that increases with milling time (up to 4 % for 15 h).

In the case of the powder mixture Fe₇₅Si₁₀Cr₁₅, after 15 h of milling, there is the formation of a solid solution of bcc structure, with an average lattice parameter of about 0.287 nm and a fcc-type solid solution. The relative composition of this last paramagnetic phase is evaluated more precisely with Mössbauer spectra and is about 17.5 %.

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