Mössbauer and xrd study of the Fe$_{0.5}$Si$_{0.5}$ system produced by mechanical alloying and sinterization

J.F. Piamba$^a$, R.R. Rodríguez$^b$, and G.A. Pérez Alcazar$^a$

$^a$Universidad del Valle, Departamento de Física A. A. 25360, Cali, Colombia.
$^b$Universidad Autónoma de Occidente, Departamento de Física, A. A. 2790, Cali, Colombia.

e-mail: jefferson.ferando33@hotmail.com

Recibido el 25 de junio de 2010; aceptado el 21 de febrero de 2011

In this work Fe$_{0.5}$Si$_{0.5}$ samples were mechanically alloyed at different milling times. The sample milled during 48 hours presents the FeSi simple cubic and the BCC Fe phases, with lattice parameters of 4.490 and 2.825 Å, respectively, then the sample alloyed during 48 hours was sintered during 72 hours and later milled at different times. After its sinterization the Fe$_5$Si$_3$ and the FeSi(SC) phases appear. When this sample is milled the FeSi(SC) structure becomes disordered with the milling time, giving place to the BCC Fe-Si disordered phase at 72 grinding hours. By Mössbauer spectrometry it was found that the milled samples present a magnetic behavior which tends to be paramagnetic at 48 hours, whereas for the thermally treated samples, as the system is disordered, it changes from paramagnetic to ferromagnetic.

Keywords: FeSi; Mössbauer spectrometry; X-ray diffraction; mechanical alloying.

En el presente trabajo se prepararon muestras de Fe$_{0.5}$Si$_{0.5}$ a diferentes tiempos mediante aleamiento mecánico. La muestra aleada a 48 horas presenta la fase FeSi cristal simple y BCC Fe, con parámetros de red de 4.490 y 2.825 Å respectivamente, posteriormente la muestra aleada a 48 fue sinterizada durante 72 horas y después molida a diferentes tiempos. Después del proceso de sinterización se encontró la coexistencia de las fases Fe$_5$Si$_3$ y FeSi(SC). Cuando esta muestra es molida, la fase FeSi(SC) se desordena con el tiempo de molienda, dando lugar a la fase BCC Fe-Si desordenada a 72 horas de molienda. Por espectrometría Mössbauer se encontró que las muestras molidas presentan un comportamiento magnético que tiende a ser paramagnético a 48 horas, mientras que para las muestras tratadas térmicamente, ya que el sistema es desordenado, cambia de paramagnético a ferromagnético.

Descriptores: FeSi; espectrometría Mössbauer; difracción de rayos-X; aleamiento mecánico.

PACS: 77.80.D; 75.40.Gb; 61.05.C.

1. Introduccion

Fe-Si alloys had been very studied due their soft magnetic character. They present high permeability and low coercive field for low Si concentrations, characteristics which make them very appropriated to produce nucleus of transformers, motors, flux multipliers and high frequency electronics devices, besides their low production costs. In order to produce these materials, different techniques had been used, one of them is mechanical alloying, technique which permits to produce amorphous and crystalline samples with nanometric size [1,2], which are used in industrial applications. Besides, this technique presents big flexibility in the process variables.

The aim of this work is the magnetic and structural properties study of the Fe$_{0.5}$Si$_{0.5}$ system, by Mössbauer spectrometry (MS) and X-ray diffraction (XRD). The samples were consolidated by MA, then they were heat treated followed by MA.

2. Experimental method

The samples were prepared by using Fe and Si powders of high purity, > 99.9 %. Samples of 3.0 grams were prepared in a high energy planetary ball mil Fritsch-Pulversette 5 at 280 rpm. The milling were conducted inside stainless steel jails evacuated at 4.5 x 10$^{-2}$ mbar, with balls of the same material inside and a mass ball to powder mass ratio of 10:1. The sintering process was realized growing the temperature until 900°C and then decreasing it until 750°C during 72 hours.

MS measurements were conducted in a conventional spectrometer with a $^{57}$Co source of 25 mCi. The Mössbauer spectra were fitted by using the MOSFIT program. The XRD patterns were registered in a Bruker D8 ADVANC diffractometer using a Cu tube and a graphite monochromator in the detector entry. The calibration sample was Si. The patterns were taken from 35.00° up to 90.00°, in steps of 0.02° each 5 seconds. The patterns were refined with the MAUD program which applies the Rietveld method.

3. Results and discussion

MA process

During the first step of the study it were prepared 7 samples of the Fe$_{0.5}$Si$_{0.5}$ system, each one of 3 grams, milled during 2, 4, 8, 12, 24, 36 and 48 hours, respectively. Figure 1 shows some representative diffractograms which represent the evolution of the system with the milling time.

The XRD patterns of the samples milled during 2 and 8 hours were refined with two phases, BCC-Fe and FCC-Si, which correspond to the primary components. The FCC-Si phase remains until 24 hours of milling, but its content decreased. This decrease was followed by the formation of a new structure, the simple cubic (CS) FeSi phase.
MÖSSLBAUER AND XRD STUDY OF THE Fe$_{0.5}$Si$_{0.5}$ SYSTEM PRODUCED BY MECHANICAL ALLOYING AND SINTERIZATION

The BCC-Fe phase remains during all the milling process, but its content decreases between 36 and 48 hours.

The lattice parameters of the different structures remain nearly constant during all the milling process, with values of 2.86 Å, 5.42 Å and 4.47 Å for the BCC-Fe, FCC-Si and FeSi(CS), respectively. The behavior of the mean crystallite size of the different phases decreases with the milling time, due the increase of the microtensions and then of their fragility. The grain size stabilizes for bigger milling times for all the samples.

Figure 2 shows the Mössbauer spectra of some samples. It can be noted a sextet which, in according with its Mössbauer parameters, can be associated to the α-Fe phase; besides, an increasing doublet which, in according with its paramagnetic character, can be associated to the FCC Si phase with some Fe atoms inside.

The spectra of samples milled between 2 and 12 hours were fitted with a sextet and a doublet. To fit the spectra of samples milled during 24, 36 and 48 hours it was necessary to use 3 sextets and a doublet. The initial sextet remains during all the milling process, and present a mean hyperfine field ($H_{hf}$) of 33.0 T. This result is in according with the XRD results, which reported the presence of the BCC Fe structure during all the milling process.

The other two sextets, obtained from 12 hours, present a mean hyperfine field of 18 T and 12 T, respectively. These fields can be attributed to Fe sites of the BCC phase which present fourth and more Si nearest neighbors. This suggest that the milling process induces disorder and due this it is possible to obtain Fe sites surrounded only by Fe atoms (sites which present a field of 33 T), and other Fe sites where some Fe neighbors are substituted by Si atoms (sites with fields smaller that 33 T).

The obtained isomer shift (IS) of the first sextet nearly corresponds to that of α-Fe and its value does not present an appreciable variation during all the process, in according with the XRD results. For the other two sextets which appear from 24 hours, it were obtained IS values which decrease from 0.078 mm/s up to -0.095 mm/s and from 0.169 mm/s up to 0.025 mm/s, respectively.

The IS of the doublet of the sample milled during 2 hours was 0.364 mm/s and decreases until 0.216 mm/s for the sample milled during 12 hours. For bigger milling times its IS value remains nearly constant with a mean value of 0.283 mm/s.

Figure 1. XRD patterns of the Fe$_{0.5}$Si$_{0.5}$ samples mechanically alloyed at different times.

Figure 2. Mössbauer spectra of the Fe$_{0.5}$Si$_{0.5}$ samples mechanically alloyed at different times.
These results permit to conclude, in accordance with the XRD results, in which a decreasing FCC-Si phase and an increasing FeSi (CS) phase were obtained, that these two phases are paramagnetic and appear in MS results as doublets with similar quadrupolar splitting (Fig. 2). The detected difference between them is the IS value, for the FCC Si phase decreases with the milling time whereas it remains nearly constant with the milling time for the FeSi (CS) phase.

Sintering process and mechanical alloying

In the second process it was prepared 40 grams of the Fe$_{0.5}$Si$_{0.5}$ sample alloyed during 48 hours, which was milled with a ball mass to powder mass ratio of 10:1, and then heat treated at high temperature. Initially the temperature of the furnace was increased until 950 °C in order to free the tensions accumulated during the milling process. After this the temperature was decreased until 750 °C in a period of 72 hours. With the last step it is expected that the sample could be homogenized and to retain the equilibrium structure at this temperature.

After the heat treatment of the material was selected 10 samples of 3 grams each one in order to be milled during 0, 0.5, 2, 4, 8, 12, 24, 34, 48 and 72 hours, respectively. Then each sample was measured by MS and XRD.

In Fig. 3 are shown the most representative patterns of this process, which correspond to the samples milled during 2, 34 and 72 hours. The other samples follow the behavior showed by these patterns.

The obtained phases after the heat treatment were the FeSi(CS) and the Fe$_5$Si$_3$. The first one remains during all the milling process and the second, which is a stable phase at high temperatures, disappears after 24 hours milling. From 34 hours the BCC Fe-Si phase appears, this is a stable phase at room temperature. It is important to note that the intensity of the first line of the FeSi (CS), which corresponds to the family planes (100) (a superlattice line) decreases with the milling time. This is an evidence of the increase of disorder of this phase.

It was found that the initial phases present decreasing values of the mean crystallite size ($\bar{O}$) as the milling time increases. The FeSi (CS) phase presents at 0 hours a size value

![Figure 3. XRD patterns of sintered and mechanically alloyed samples of the Fe$_{0.5}$Si$_{0.5}$ system.](image)

![Figure 4. Mössbauer spectra of sintered and mechanically alloyed samples from 0 to 72 hours.](image)
of 104 nm and finish with a value of 14 nm at 72 hours. The Fe$_5$Si$_3$ phase presents a similar behavior with an initial value of $\Phi$ corresponding to 64 nm and ending at a value of 6 nm for 24 hours. For the BCC Fe-Si phase presents a nearly constant value of $\Phi \approx 10$ nm. These results reflect the fracture process induced by the MA technique and the instability of the Fe$_5$Si$_3$ phase which disappears after 24 hours milling.

The results of the volumetric fraction show that the FeSi(CS) phase remains nearly constant with a value of 0.76 until 34 hours and then decreases up to 0.32. The corresponding values of the Fe$_5$Si$_3$ structure remain nearly constant with a value of 0.24 until 24 hours and then disappear. Finally the BCC Fe-Si phase is detected at 34 hours and increases its volumetric fraction up to a value of 0.68 for 72 hours. As can be noted the BCC Fe-Si phase increases.

The lattice parameters of the different phases remain nearly constant during all the milling process. The lattice parameter of the FeSi (CS) phase presents a value around 4.93 Å. Those of the Fe$_5$Si$_3$ phase, which has a hexagonal structure, are $a = 6.763$ Å and $c = 4.734$ Å, and that of the BCC Fe-Si is 2.816 Å.

In Fig. 4 is shown Mössbauer spectra of some samples sintered and then milled at different times. The spectra of samples milled during 0 up to 24 hours were fitted with two sextets and two doublets. For samples milled during 34, 48 and 72 hours their spectra were fitted with an increasing Hyperfine Magnetic Field Distribution (HMFD) with 8, 12 and 16 subspectra, respectively; and two doublets, one of them with a decreasing spectral area.

The hyperfine field of one sextet varies around 16.5 T, whereas that of the other sextet around 14 T. These values are in accordance with those reported for the Fe$_5$Si$_3$ phase [7]. This assumption is confirmed in current work by the fact that these sextets disappear after 24 hours and by the XRD results which show that the Fe$_5$Si$_3$ phase disappear after 24 hours milling. The previous assumption permits to conclude that the two doublets can be associated with the FeSi (CS) phase and the HMFDs to the BCC Fe-Si phase. From the obtained results the variation of the fields of the two sextets and of the mean hyperfine field of the HMFD as a function of the milling time was plotted and showed in Fig. 5. The last three points of Fig. 6 correspond to the mean values of the HMFDs, and they are 18, 15 and 16 T, respectively.

The fact that the BCC Fe-Si phase, which appears for more than 24 hours milling, presents an increasing HMFD shows that it is ferromagnetic and disordered, and that this disorder increase with the milling time.

The IS of the first doublet is nearly constant and its value is around 0.456 mm/s, whereas the IS of the second doublet decreases from 0.335 mm/s for 0 hours up to 0.230 mm/s for 72 hours.

The Mössbauer parameters obtained for the second doublet, which was associated to the FeSi (CS) phase, is in accordance with the reports of Lie Tie et al. [5] and R. R. Rodríguez [6]. They reported this phase for alloys of the Fe-Si system prepared by MA.
4. Conclusions

In the first part of this study, samples of Fe$_{50}$Si$_{50}$ were produced by MA. The presence of BCC (Fe-Si), FCC (Si-Fe) and FeSi(CS) phases was detected. The first one decreases with the milling time but remains until 48 hours; the second one decreases with the milling time and disappears after 24 hours; and the third appears at 12 hours and increases with the milling time. Mössbauer spectrometry measurements of these samples showed that the FCC (Si,Fe) and FeSi(CS) phases are paramagnetic and appear as a similar doublet, and that the BCC (Fe,Si) phase is ferromagnetic.

In the second part of this work samples of the Fe$_{50}$Si$_{50}$ system were milled during 48 hours, heat treated at high temperature and then milled during several times. The XRD results permit to detect the FeSi(CS), Fe$_5$Si$_3$ and BCC Fe-Si phases. The first two phases are obtained after the sintering process. When the milling process is conducted the phase Fe$_5$Si$_3$ disappears after 24 hours milling and then the BCC Fe-Si phase appears. The Mössbauer results permit to prove that the FeSi(CS) phase is paramagnetic and appears as two doublets. One of these doublets decreases with milling time after 24 hours of milling. The Fe$_5$Si$_3$ phase is ferromagnetic and appears as two sextets. The BCC Fe-Si phase is ferromagnetic and disordered and appears as an increasing HMFD.

Acknowledgements

The authors would like to thank Colciencias, Colombian Agency, CENM and Universidad del Valle for the financial support given this work.