ENHANCED BINOMIAL METHOD FOR HYPERFINE FIELD DISTRIBUTIONS OF THE MECHANICALLY ALLOYED Fe-Si SYSTEM

H. Sánchez Sthepa[1], J. Restrepo[2], M. Fajardo[3], G. A. Pérez Alcázar[3], and R. Rodriguez[3]
[1] *Escuela de Ingeniería de Materiales, Universidad del Valle, Cali, Colombia*
[2] *Departamento de Física, Universidad de Antioquia, Medellín, Colombia*
[3] *Departamento de Física. Universidad del Valle, Cali, Colombia*
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ABSTRACT

$Fe_{1-q}Si_q$ alloys, with $0.03 \leq q \leq 0.3$, were prepared employing mechanical alloying with milling times ranging from 15 to 75 hours. Magnetic and structural properties of the samples were followed by means of ^{57}Fe Mössbauer spectroscopy and X-ray diffraction. The hyperfine field distributions obtained from fitting the Mössbauer spectra were modeled by using an enhanced binomial method, which includes a new parameter accounting for the different degrees of disorder that the milling procedure can induce. The method employed allows obtaining both, the most probable configurations as well as the hyperfine field fractional changes originated by the atomic environment within the first three Fe coordination shells as the silicon concentration is increased. Results involving compositional and milling time dependence of the Mössbauer parameters and those used in our model are also presented and discussed.

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RESUMEN

Las aleaciones de $Fe_{1-q}Si_q$, con $0.03 \leq q \leq 0.3$, fueron preparadas empleando la aleación mecánica con tiempos en el molíenda que se extendieron a desde 15 horas hasta 75 horas. Las características magnéticas y estructurales de las muestras fueron estudiadas por medio de la espectroscopia Mössbauer de ^{57}Fe y de la difracción de rayos X. Las distribuciones hiperfinas del campo obtenidas de los espectros Mössbauer fueron modeladas usando un método de expansión binomial que incluye un nuevo parámetro que explica los diversos grados de desorden que el procedimiento de molienda puede inducir. El método empleado permite el obtener ambos, las configuraciones más probables así como los cambios fraccionarios del campo hiperfino originados por el ambiente atómico dentro de las primeras tres cáscaras de la coordinación del FE mientras que se aumenta la concentración del silicio. Los resultados implican la composición y la dependencia del tiempo de los parámetros Mössbauer que son usados en nuestro modelo también se presentan y se discuten.

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1. Introduction

The Fe-Si system has been widely studied because of the importance of some of its alloys depending on composition, to be used as soft magnetically materials, particularly those with 3.5 wt. % (6.73 at. %) and 6 wt. % (11.26 at. %), which are used as cores of common and high power transformers, respectively. These so-called electric steels are produced through melting processes but their brittle character increases with the silicon content. On this last respect, the mechanical alloying technique allows considering a wide range of compositions for producing these types of alloys [1,2] with the advantage that brittleness can be ignored no matter the sili-

con content is. Additionally, in order to determine the structure and to evaluate the magnetic properties of this system, X-ray diffraction (XRD) and Mössbauer spectroscopy techniques have been usually employed [3, 4] from which some restricted binomial models based on the idea of a homogenous and random atomic distribution to interpret the experimental hyperfine field distributions (HFDs) have been proposed [4, 5, 6].

In this work, we present a new enhanced binomial distribution method to compute HFD applied to the study of Fe-Si disordered alloys. The employed model takes into account the contributions of first, second and third nearest neighbors. On the other hand, since the mechanical alloying can result in the introduction of different kinds of disorder, we introduce a new parameter dealing with this feature. Experimental HFDs were obtained by fitting the Mössbauer spectra according to the disordered character of the samples whereas the coordination numbers employed in the model are consistent with the XRD patterns.

2. Experimental

The samples were prepared from pure element powders (Fe 99.9% and Silicon 99%). We used a "pulverisette 5" planetary high energy ball mill. The speed used was 280 rpm, and the milling was carried out using a sequence of 60 minutes milling and 30 minutes resting. The samples were weighted, in the stoichiometric relation and mixed in a small flask, then transferred to the vials, vacuumed and filled with argon. We used a ball mass to powder mass relation of 10:1. The milling times were: 15, 30, 50 and 75 hours.

3. Model

Random configurations of Fe and Si atoms in a BCC crystalline lattice for a silicon concentration up to 25 at % and FCC for 30 at % Si according to XRD analysis were implemented. In the frame of a pure binomial atomic distribution the probability function for having certain configuration (n_1, n_2, n_3), where each n_k corresponds to the number of Si atoms in the k^{th} coordination shell, is given by the following expression:

$$P(n_1, n_2, n_3) = C_{N_1}(n_1) C_{N_2}(n_2) C_{N_3}(n_3) q^{\sum n_i} p^{\sum (N_i - n_i)} \tag{1}$$

where the terms of the form $C_{N_k}(n_k) = N_k!/n_k!(N_k - n_k)!$ are the binomial coefficients representing the number of possible configurations for which n_k atoms can be located in N_k available sites. N_1=8, N_2=6 and N_3=24 are the coordination numbers for the first, second and third coordination shells, respectively, in a BCC lattice. Analogously, N_1=12, N_2=6 and N_3=12 for a FCC lattice, and each n_k runs from 0 up to N_k. The silicon concentration is "q" and that of the iron is "p", obeying the relationship $p + q = 1$. In order to take into account the effect of the preparation method, upon the disorder of the system, which now can involve for instance a random distribution of vacancies, defects as well as distortions originated by the milling process in addition to atomic disorder, we introduce a new parameter ξ. Such parameter must be dependent on those preparation methods inducing disorder as well as on the milling time. Moreover, when vacancies and defects are taken into account the effective number of Si atoms within the first three coordination shells must be affected. This fact enables to introduce the following probability distribution for which the pure binomial method is a particular case with $\xi = 0$:.

$$P^*(n_1, n_2, n_3) = Z^{-1} \prod_i^3 C_{Ni}(n_i) q^{(1-\xi)\sum n_i} p^{\sum (N_i - n_i)} \text{ with } Z = \sum_{(n_1, n_2, n_3)} q^{-\xi \sum n_i} P(n_1, n_2, n_3) \tag{2}$$

The expression employed to estimate the B_{hf} take into account the milling time τ in the following way [7]:

$$B_{hf}(n_1, n_2, n_3) = B_0(1 - \alpha n_1 - \beta n_2 - \gamma n_3 - \lambda \tau) \tag{4}$$

where B_0=33 T is the pure Fe hyperfine field value temperature, and $\lambda = (\partial B_{hf} / \partial \tau) B_0^{-1}$ represents the fractional change of the hyperfine field per milling time unit; the fit parameters α, β, and γ can depend on composition and correspond respectively to the field fractional changes per solute (Si) concentration unit in the first, second and third Fe coordination shell as the silicon content is increased. In particular, α would be given by $\alpha = (\partial B_{hf} / \partial n_1) B_0^{-1}$. Hyperfine field distributions are obtained by considering equations (2) and (4), whereas the mean hyperfine field (MHF) is computed according to:

$$\langle B_{hf} \rangle = \sum_{n_1} \sum_{n_2} \sum_{n_3} P^*(n_1, n_2, n_3) B_{hf}(n_1, n_2, n_3) \tag{5}$$

4. Results and discussion

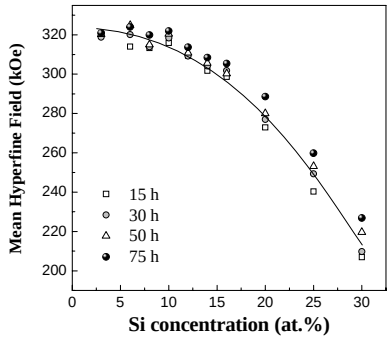

Figure 1. MHF as a function of the silicon concentration.

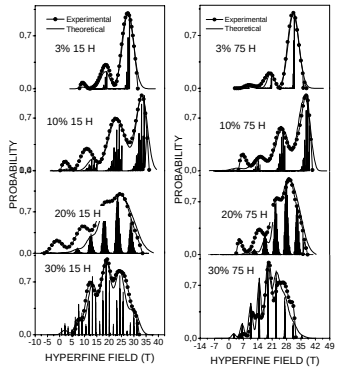

Figure 2. Experimental and theoretical HFDs for Fe-Si system

Figure 1 shows that the MHF decreases in a well-behaved fashion as the Si content is increased. This behavior reflects the dilutor character of the Si atoms. Moreover, results suggest a slight dependence of the MHF on the milling time, which motivated the inclusion of the λ parameter in our model. Figure 2 shows the experimental and theoretical HFDs corresponding to the highly diluted samples (3, and 10 at. % Si), for 15 and 75 hours of milling. Similar results were obtained for the intermediate compositional and milling times. As it can be observed from this figure, the employed enhanced binomial method reproduces quite well the experimental HFD for which a well-defined structure of three remarkable peaks is preserved in this low Si concentration regime. In this case, the obtained ξ and λ values (close to zero) suggest the existence of homogeneous atomic disorder independent on the milling time, as is expected for diluted system. These results are in agreement with the presence of an **A2** disordered phase [8]. The α, β and γ values in the low Si regime (up to 10 at. %), remain practically constant at around 0.08, 0.002 and 0.004, respectively. The obtained α value implies that the substitution of one Fe atom

by Si in the first Fe neighborhood involves a HF reduction of 2.6 T, whereas such substitution in the second and third Fe coordination shells and within the estimated error bars should give rise to a reduction of the order of 0.1 T.

Results for samples with Si concentrations above 10 at. % reveal discrepancies (Fig. 2) between the experimental and the binomial HFD, which are more evident as the silicon concentration increases. However these discrepancies become relevant at lower hyperfine field values where the configurations (n_1, n_2, n_3) are characterized by a greater amount of Si atoms favoring the formation of clusters.. Additionally, to interpret the discrepancies must be taken into account that the lattice parameter ***a*** varies with composition and with a tendency to be smaller, affecting the exchange energy $J_{Fe\text{-}Fe}$ [9], and the possible presence of an ordered phase **B2,** accordingly with the equilibrium phase diagram [10], which although appears at about 750°C [4] through melting process, it could be also induced by means of the mechanical alloying method.

Finally, for the 30 at % Si sample, results reveal a structural transition from **A2** to a FCC phase. By considering the respective coordination numbers of a FCC lattice we obtained the corresponding HFD which is compared to the experimental one in Figure 2. The agreement is reasonable at low milling times.

5. Conclusions

The proposed enhanced binomial method seems to be a suitable tool in interpreting the hyperfine field distributions of mechanically alloyed Fe-Si disordered alloys. Results allow distinguishing two compositional regions: a) the first at Si concentrations below 10 at. % for which the response functions α, β, and γ, are practically constant from which the main contribution to the hyperfine reduction comes from the first Fe coordination shell giving rise to a good agreement between the experimental and the binomial HFDs; and b) the second at Si concentrations above 10 at. % for which there is a strong dependence of the mentioned response functions. Discrepancies in this regime are attributed to the limitations of the model and to a greater complexity of the system concerning the degree of disorder. Finally, the influence of the milling time in the HFD, represented by the λ parameter, becomes evident only at higher Si concentrations with a tendency to decrease the MHF as the milling time is increased, whereas below 15 at. % Si, the magnetic properties of the system seem to be independent on the milling time.

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Referencias

[1] García Escorial, A., Adeva, P., Cristinan, M.C., Martín, A., Carmona, F., Cebolleda, F., Martín, V.E., Leonato, M. and González, J.M., Mater. Sci. Eng. A134 (1991), 1394.
[2] Kuhrt, C. and Schultz, L., IEEE Trans. on Magn .29 (1993), 2667
[3] Sánchez Sthepa, H., Fajardo, M. and Pérez Alcázar, G.A., Hyp. Int. 122 (1999), 115
[4] Abdellaoui, M., Gaffet, E. and Djega-Mariadassou, C., Mater. Sci. Forum 179 (1995), 109.
[5] Restrepo, J., Pérez Acázar, G.A. and Bohórquez, A., J. Appl. Phys. 81 (1997), 4101
[6] Sánchez, H., Restrepo, J., Fajardo, M. and Pérez Alcázar, G.A., Phys . Stat. Sol. (b) 220 (2000), 347
[7] Fujita, E., Mössbauer Spectroscopy, Topics in Applied Physics (Springer, Berlin, 1975), Vol 5, p. 201
[8] Degauque, J., Bouchara, D., Fagot, M., Bras, J., Redoules, J.P., Chomel, Ph. and Astle. B., IEEE Trans. on Magn. 26 (1990), 2220.
[9] Cullity, B.D., Elements of X-ray diffraction. Addison-Wesley Publishing Company (1967) p.134.
[10] Smithells, C.J., Metals Reference Book. ed. Butterworths. (London and Boston 1978) p. 615.