Effect of boron in $Fe_{70}Al_{30}$ nanostructured alloys produced by mechanical alloying

M. M. Rico · G. A. Pérez Alcázar · J. M. Greneche

Abstract The substitution of aluminum by boron in the $Fe_{70}Al_{30}$ system prepared by high energy ball milling is studied when the B content ranged from 0 up to 20 at. %, and the milling times were 24, 48 and 72 h. X-ray diffraction (XRD) patterns of $Fe_{70}Al_{30}$ showed a predominant bcc structural phase with a lattice parameter larger than that of α-Fe. A second (tetragonal) phase arose with the addition of boron. It is associated to the existence of $(Fe, Al)_2B$, although the values of the lattice parameters are slightly different from those found in the literature. This phase shows high stability; its lattice parameters and the Mössbauer parameters do not show notable variations, either with milling time or composition. It was also evidenced that an increase of boron content and of milling time produced a decrease of the lattice parameter of the Fe-Al bcc structure. This is in agreement with the small atomic radius of boron in comparison with that of aluminum. This also allows boron to occupy interstitial sites in the lattice, increasing the grain size and giving rise to the ductile character of the alloy. On the other hand, 300 K transmission Mössbauer spectra (TMS) were fitted, for low boron concentrations (<8 at.%), with a hyperfine field distribution (HFD) associated with the bcc phase. For high boron content (≥8 at.%), a magnetic component related to the tetragonal phase is added and its broadened lines are attributed to the disordered character of Fe_2B, probably induced by the milling process.

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1 Introduction

It has been well established that high-energy mechanical milling is one of the best techniques for producing nanostructured powders [1, 2]. This method consists in the mixing of powders (of different metals or alloys/compounds), which are milled together to get a homogeneous alloy through successive welding and fracture processes [3]. The nanostructured powders obtained consist thus of particles composed of nanometer size crystalline grains, linked to one another through grain boundaries [4]. The reduction of the grain size improves the physical, mechanical and magnetic properties of the material [3]. For this reason nanostructured materials are potentially attractive for many applications [5].

This is particularly evident in the case of Fe-Al intermetallic systems. The dependence of the magnetic properties on the state of disorder and the microstructure makes this system interesting to study when it is produced by the mechanical alloying (MA) process.

The Fe-Al intermetallic compound possesses advantageous properties, in particular a high specific strength (strength-to-density ratio), good strength at intermediate temperature and an excellent corrosion resistance at elevated temperatures under oxidizing, carburizing and sulfidizing atmospheres. These features make the Fe-Al intermetallic compounds very attractive materials for structural and coating applications at elevated temperatures in hostile environments [6]. The addition of small amounts of boron to Fe-Al can change the fracture mode from intergranular failure to transgranular fracture. This change in fracture mode is believed to result from the segregation of boron to grain boundaries. Studies on the microstructure of these alloys gave evidence that the addition of boron can also result in the formation of Fe_2B precipitates and a tetragonal phase which is likely coherent with the matrix [7].

A recent study [4] showed that the addition of boron (up to 20 at. %) to the Fe-Al system produces growth of the grain boundaries giving rise to a low hyperfine magnetic field contribution that can be attributed to iron atoms located in them. However, there are few reports to our knowledge on the magnetic properties of ternary FeAlB alloys [4, 8, 9]. The purpose of the present investigation is to obtain a better understanding of the evolution of mechanically alloyed $Fe_{70}Al_{30}$ system with milling time and the effect of the addition of boron in its structural and magnetic properties. Both variations in particle size and in lattice parameter have been determined through X-ray diffraction studies. The magnetic hyperfine field distributions obtained from ^{57}Fe Mössbauer spectra have been used to identify the different magnetic phases that appear.

2 Experimental section

Fe, Al and B powders with 99.9 % purity were used to prepare samples of $Fe_{70}Al_{30-x}B_x$ ($0 \leq \times \leq 20$) by mechanical alloying. The powders were milled for 24, 48 and 72 h in a planetary milling (Fristch Pulverisette 5) using hardened stainless

steel vials together with balls of the same material, under vacuum. The ball-to-powder mass ratio was 15:1. A structural characterization was carried out with X-ray diffraction (XRD) using a Philips X'pert diffractometer (with monochromatized Cu Kα radiation; $\lambda = 1.54056$ Å). The patterns were then refined by the Rietveld method using the MAUD program, which is combined with Fourier analysis to describe the broadening of the Bragg peaks [10]. The magnetic characterization was carried out by transmission Mössbauer spectrometry (TMS) by means of a conventional constant acceleration spectrometer while the spectra were fitted by using the MOSFIT program involving discrete distributions of magnetic and/or quadrupolar components with lorentzian lines [11].

3 Results and discussion

Figure 1 shows XRD patterns for samples of $Fe_{70}Al_{30}$ and $Fe_{70}Al_{10}B_{20}$ milled for 24 and 72 h. The sample without B evidences characteristic lines of a bcc structure, coming from the bcc character of pure iron, whereas the samples with B concentration higher than 4 at. % exhibit both bcc and tetragonal phases. This last phase appears as a consequence of Fe and B alloying in a Fe_2B–like phase. The XRD patterns were fitted by means of the Maud program [10] and the results are presented in Fig. 2a (bcc phase) and b (tetragonal phase). The lattice parameter for the bcc phase has a higher value than that of bcc Fe, because of the presence of Al, which has a larger atomic radius. However, this parameter decreases when the B concentration increases, since some Al atoms are substituted by B (which is much smaller than both Al and Fe atoms). This substitution, together with milling time, helps to bring the diffraction planes nearer, which in turn contributes to decrease the lattice parameter. In the case of the tetragonal phase, there is no apparent dependence of lattice parameters on either boron concentration or milling time. Nevertheless, a slight variation of these parameters was observed in comparison with those of pure Fe_2B. It can be attributed to the inclusion of Al atoms in the positions of Fe (0.1649; 0.1649; 0). The grain size for the bcc phase ranges from about 10 to 29 nm, and decreases when the B concentration increases, because B atoms occupy interstitial sites in the bcc phase, producing a growth of grain boundaries [12]. On the other hand, there is no clear behavior with milling time. Nonetheless, for B concentrations between 15 and 20 at. %, there is a substantial reduction of the grain size between 24 and 48 h, as it is observed in Fig. 2a (middle). This is a consequence of the increase of grain boundaries with milling time; this effect tends to stabilize for 15 and 20 at. % of B, starting from 48 h, where the grain size remains rather constant. For the tetragonal phase, no tendency is found for low concentrations of boron. For higher B contents (15 and 20 at. %), closely similar values for grain size were obtained.

The bcc and tetragonal phase contents are shown at the bottom of Fig 2a and b, respectively. An increase of the tetragonal phase is observed with B content, being higher for 48 and 72 h. Despite that this value is strongly increased with milling time, it is not higher than that reported for $Fe_{60}Al_{20}B_{20}$ alloys at the same milling time [4].

Figure 3 shows 300 K Mössbauer spectra for samples milled for 24 and 72 h. For the sample without B a characteristic spectrum of a disordered magnetic system is observed. The appearance of this spectrum suggests a fit with a hyperfine field
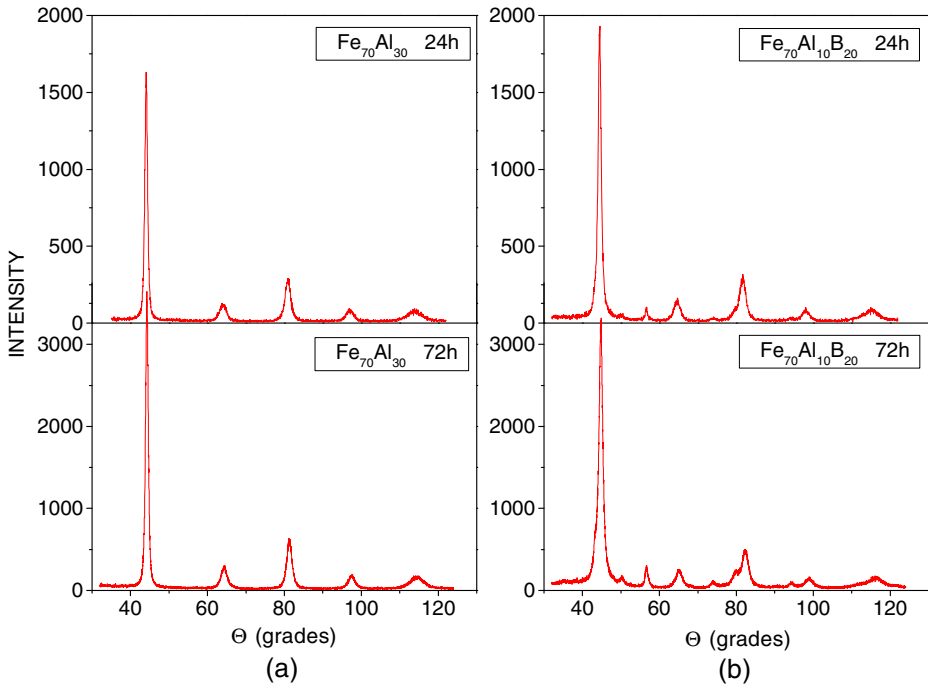
Fig. 1 X- Ray diffraction patterns for samples of $Fe_{70}Al_{30}$ (**a**) and $Fe_{70}Al_{10}B_{20}$ (**b**) milled for 24 and 72 h

distribution (HFD) associated to the bcc-disordered phase. It can be noted that all the spectra show an asymmetry which was reproduced in the spectra by fitting them with a distribution of IS. When milling time increases, the spectral lines are more separated and narrowed. This means that the HFD reaches more elevated field values with higher probabilities as illustrated in Fig. 4a, which shows the HFDs for samples without B (pure $Fe_{70}Al_{30}$ samples) for different milling times.

This enhancement of the HF values and the decrease of the lattice parameter (Fig. 2a) is in agreement with the reported results for milled $Fe_{60}Al_{40}$ samples [13, 14]. It can also be observed that the effect of milling time is to increase both the probability and the field of the most intense peak, and to decrease the probability of the peaks at small fields, giving rise thus to an increase of the MHF. This behavior was also reported by different authors for this type of alloys [15, 16], who attributed it to the increase of the disorder. Besides, the increase of the ferromagnetic behavior with the disorder was also reported in arc-melting [17] and MA [13] produced FeAl disordered crystalline alloys.

When B is added (Fig. 3b) the spectra were also fitted with HFD, but some new lines appear like a sextet that are attributed to the ferromagnetic Fe_2B tetragonal phase. These lines become more intense when milling time increases. However, this second phase was detected at 48 and 72 h for 10 at. % of B content and from 24 h for higher concentrations. In the case of $Fe_{70}Al_{10}B_{20}$ milled for 72 h, a first naive but rather good description is obtained by means of only two magnetic components with broadened lorentzian lines and a doublet: the hyperfine field values of the magnetic
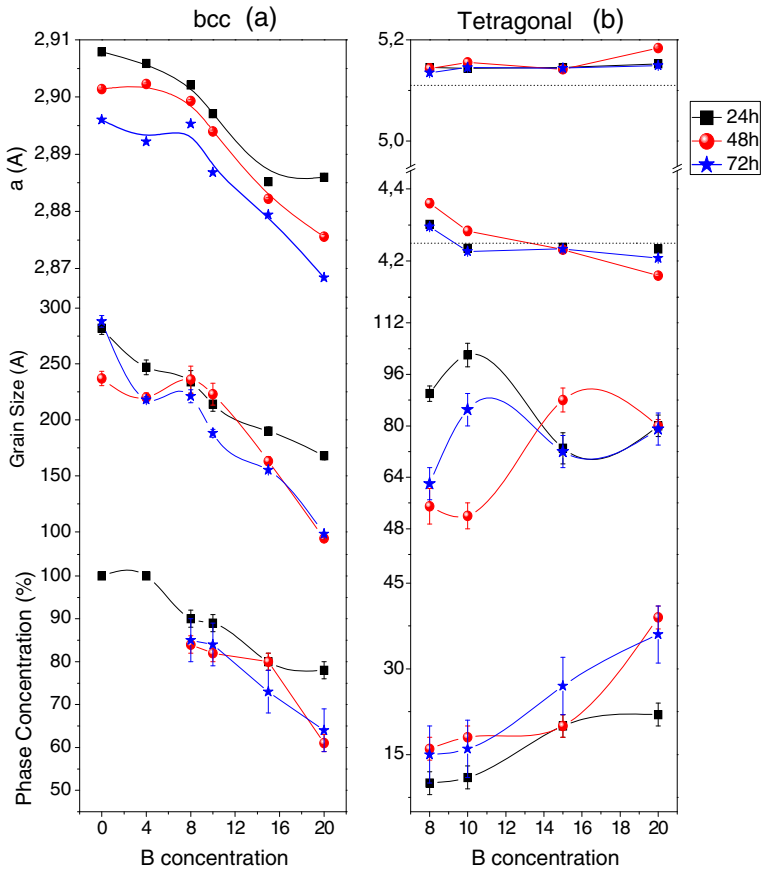
Fig. 2 Mean structural parameters as a function of B concentration obtained from XRD patterns for different milling times: lattice parameter, grain size and weight fraction of bcc (**a**) and tetragonal (**b**) phases

components are found close to 33 T and 23.4 T, and allow these 2 components to be assigned to bcc-Fe rich and tetragonal Fe_2B phases, respectively. Figure 3b-right corresponds to this fit. The modeling can be improved by considering a distribution of hyperfine fields for the first component. Then the second Mössbauer component was better described by means of two magnetic sextets associated with two hyperfine field values of 22,9 and 24,0 T, in rather good agreement with that of the pure Fe_2B phase [18]. Such a model was successfully achieved for all Mössbauer spectra with B concentration of 20 at. %. The doublet is attributed to those Fe sites of the bcc phase rich in Al atoms, which appear when some Fe atoms of the bcc phase migrate to form the Fe2B phase.

In order to see the effect of the increase of boron concentration and the effect of milling time in samples with and without B, the HFDs for 0 and 20 at. % B milled at different times are illustrated in Fig. 4. It can be noted that the addition of B tends to shift the HFDs to higher fields, and allows the observation of two regions with more clarity: the first one in the higher field range, which gets narrower and achieves higher
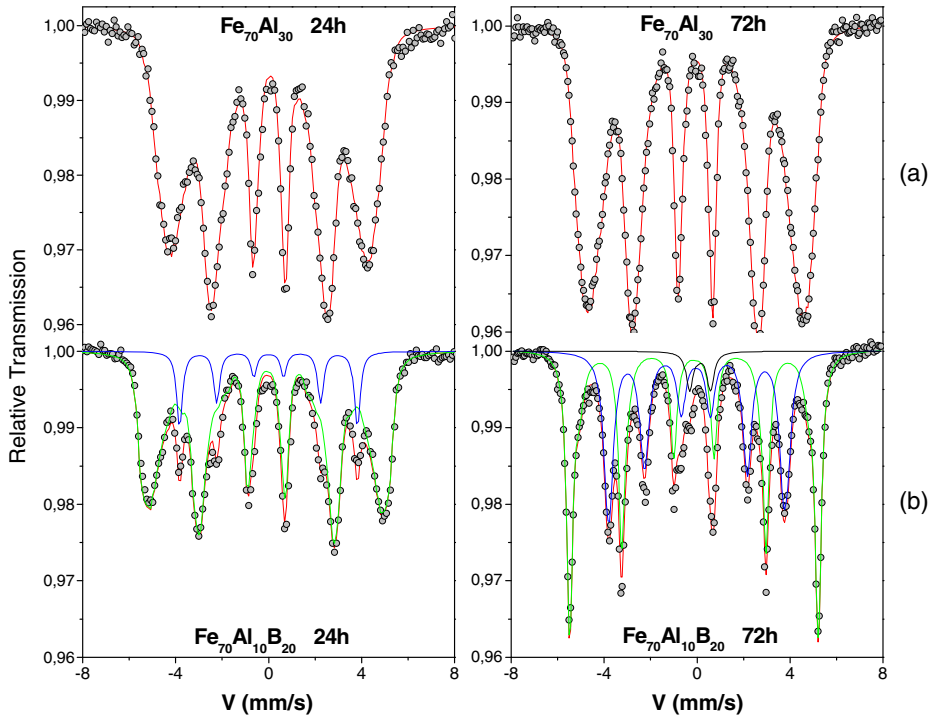
Fig. 3 Mössbauer spectra at room temperature for samples milled for 24 and 72 h

probabilities as B content increases, while the second one lies in the lower field range with lower probabilities. It should be noted that those low fields are slightly higher than those observed for the samples without B. Otherwise, the increase of milling time in both type of samples gives rise to the increase of the probability and the narrowing of the most intense peak, accompanied by the disappearing of one of the small peaks and the increase of the probability of the other. This narrowing is associated with the increase of the disorder of the samples due to the tendency to obtain chemical equilibrium. This chemical equilibrium homogenizes the samples decreasing in this way the concentration gradients and carrying the distribution around of only one more probable Fe site. It can be also seen that when the boron contents increases the HFDs become narrower, and this can be explained as a consequence of the formation of the Fe_2B phase. Then some iron atoms are lost from the bcc phase in order to form the new one and in this way there are less environments in the HFD of the bcc phase.

In Fig. 5 the behavior of Mössbauer parameters with boron content and milling time is observed. The isomer shift (IS) of the HFDs, at top of Fig. 5, diminishes with B concentration for 24 h of milling time. This diminution is associated with the increase of s electrons in the nuclei of Fe atoms due to penetration of boron atoms in the bcc phase. At 48 h and 72 h, the IS is approximately constant, with practically no influence of concentration. The meaning of this behavior is that for these alloys a saturation stage is reached which is not sensitive any more to longer synthesis times and there is consequently a saturation of the s electron density in the nuclei of the Fe atoms. The IS for the tetragonal phase of the sample milled during 24 h behaves
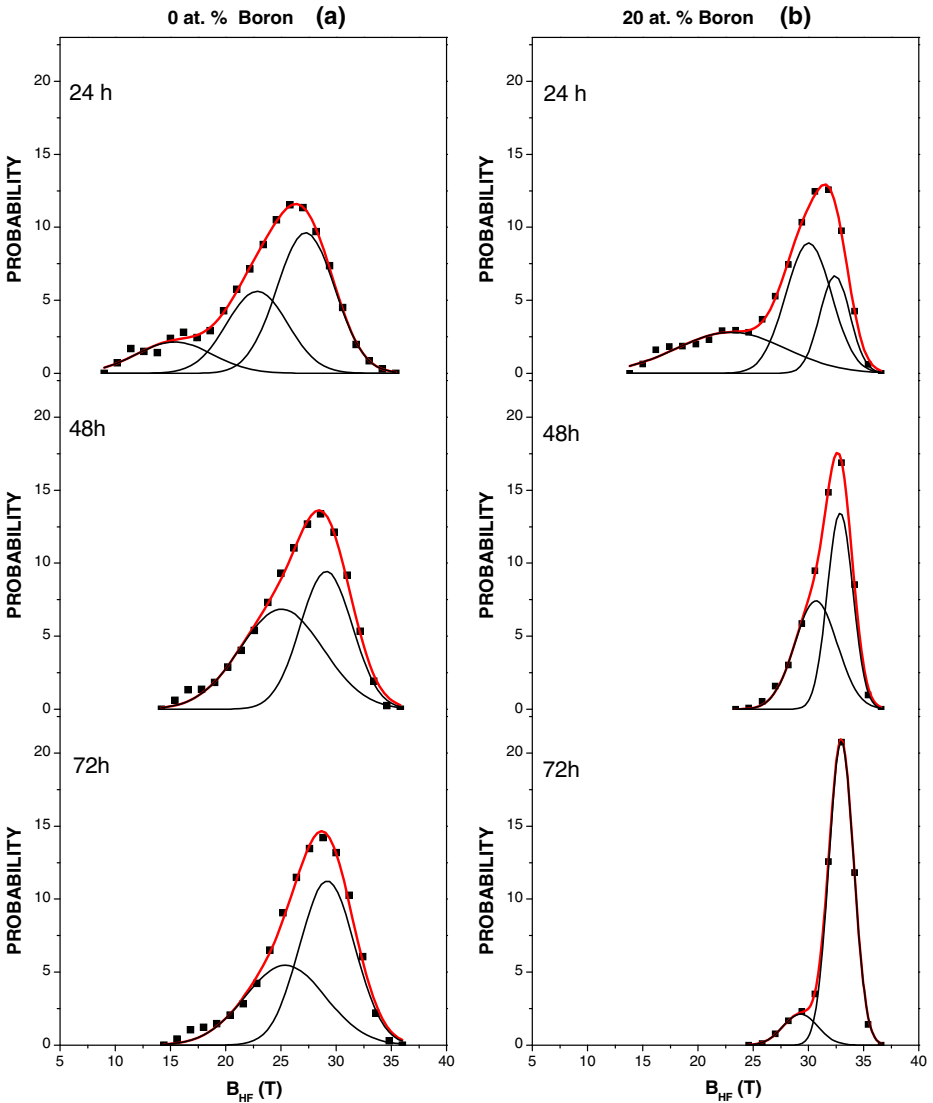
Fig. 4 Hyperfine field distribution and Gaussian fits for samples without B (**a**) and with 20 at. % of B (**b**), milled for 24, 48 and 72 h. All measures were taken at 300 K

in the range previously reported in literature for melted Fe_2B alloys [18]. For 48 h and 72 h this parameter shifts to values smaller than the lower limit, remaining nearly constant with B concentration.

Figure 5 (middle) shows the behavior of the MHF for the bcc phase and the HF of the Fe_2B phase. For the sample without boron the MHF increases with milling time tending to a constant value. At 24 h, the MHF is almost constant. For 48 h and 72 h when boron content increases these MHF values get lower as a consequence of the migration of the Fe atoms to the other phase and the decreasing of the local
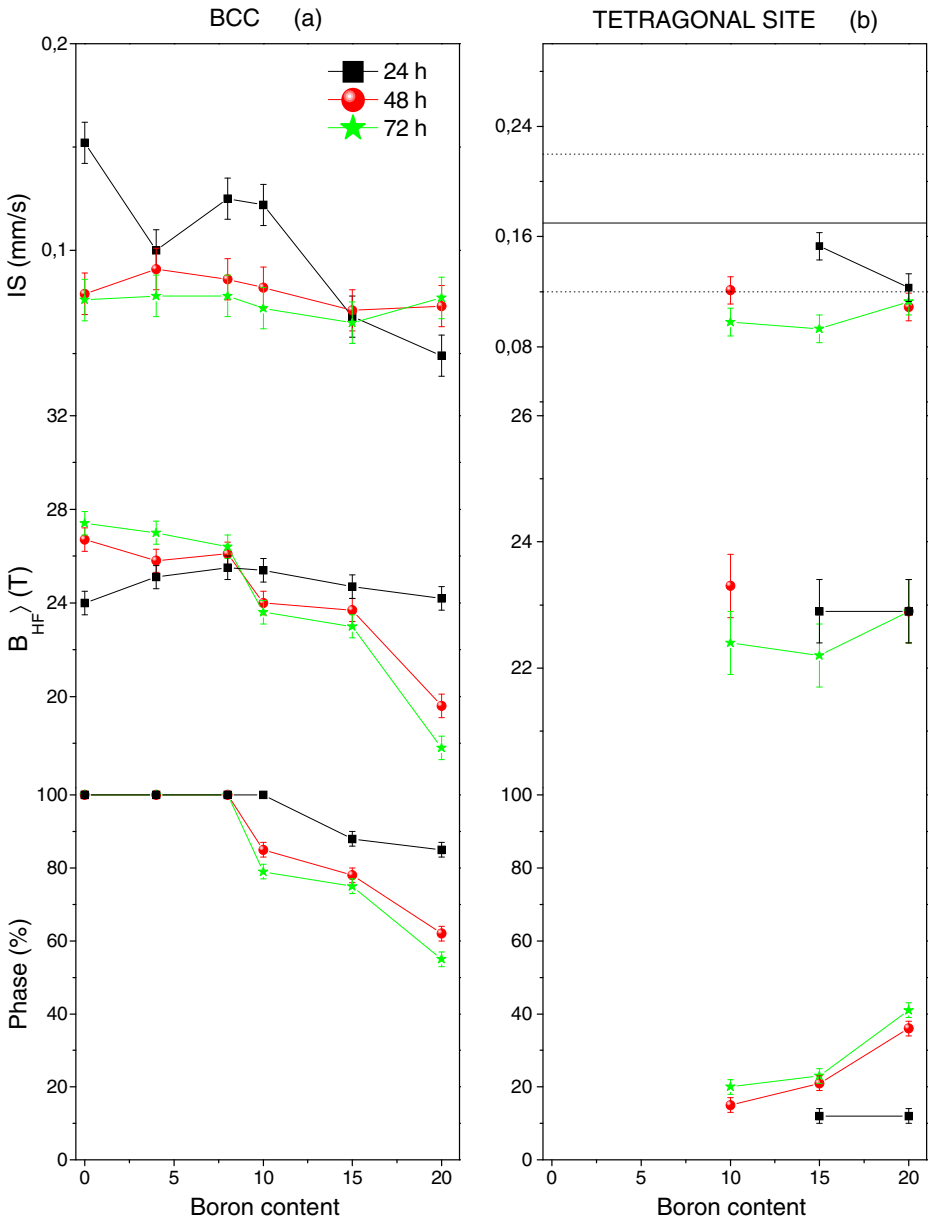
Fig. 5 Mössbauer parameters obtained. Isomer shift (**a**) MHF (**b**) and phase percent for the field distribution (**a**) and the tetragonal site (**b**)

magnetic moment of iron due to the increase of the nearest neighbors Al atoms [19, 20]. Besides, for these milling times, for each B concentration, the MHF values are very similar, which confirms that synthesis time has been reached at 48 h. The HF for the tetragonal phase for all milling times tends to coincide with the values found for 20 at. % of boron.

Figure 5 (bottom) depicts the proportion of Fe atoms that make part of the field distribution and the ferromagnetic site. It can be observed that the number of Fe atoms of the tetragonal phase increases with both milling time and boron concentration. This is in agreement with the XRD results shown in Fig. 2.

4 Conclusions

The effect of inclusion of boron and milling time in the FeAl mechanical alloying system was studied through XRD and MS. It was found that when the boron content increases, a bcc phase associated to Fe-Al tends to coexist with a tetragonal phase related to Fe_2B-like phase.

For B concentrations from 0 up to 10 at. % the Mössbauer spectra were fitted with a distribution that is characteristic of a disordered system which is associated with the bcc phase. For B contents higher than 10 at. %, the distribution becomes narrower and it was necessary to employ ferromagnetic sites with HF values close to those reported for pure Fe_2B.

Both, the increase of boron concentration and the milling time induce the narrowing of the HFD. The first one is a consequence of the loss of iron atoms from the bcc phase, which migrate to form the Fe2B phase; and the second one is due to the increase of the disorder. The paramagnetic site, which appears at 20 at. % B and 72 h of milling, corresponds to bcc Fe sites rich in aluminum.

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