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Amorphization of ErFe₂ obtained by milling under different atmospheres

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Abstract. In the present work, high-energy milling under two different atmospheres was applied to the ErFe₂ intermetallic compound and to the chemical elemental powders of Er and Fe with ErFe₂ stoichiometric composition. Sample A is the compound milled under Ar, sample B the compound milled under N₂ and sample C the elemental powders milled under N₂ atmosphere. X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) results of the samples A and B show a segregation process with increase of the milling time. Under N₂ atmosphere, the initial compound was nearly dissociated with 50 h of milling, while with Ar atmosphere the segregation process was completed with 100 h of milling. From the analysis of the XRD and MS results, it was possible to observe the appearance of other phases at intermediate milling times, in both samples A and B. One phase was associated with an amorphous ErFe₂ alloy with a magnetic ordering temperature, obtained by AC magnetic susceptibility, at about 190 K, a second phase was attributed to nanocrystallites of α -Fe and a third one associated with an fcc Er high-pressure phase stabilized by N atoms. In the case of sample B, for milling times longer than 400 h, XRD and MS results indicate the presence of an Fe–Er–N disordered alloy, with magnetic ordering temperature above room temperature. The XRD and MS results of sample C show the formation of an ErFe₂ amorphous phase, with about 87% of MS relative area in this phase at 68 h of milling.

1. Introduction

Over the past decade, high-energy milling (HEM) has been shown to be an important technique in powder metallurgy. Some of the most usual applications of this method involve the preparation of materials with distinct physical properties, i.e. materials with metastable phases, or just new materials. In the field of new materials, amorphous phases obtained from the HEM of intermetallic compounds have been extensively studied by Larica *et al* (1995), Biondo *et al* (1997), Xia *et al* (1996) and Zhou and Bakker (1994a, b). It has been found that besides the thermodynamic aspects of the materials under preparation, specific milling conditions are also very important in order to obtain such phases. These conditions can be summarized as the ball to powder volume ratio, local atmosphere and temperature, quality of the milling tools and the milling energy employed. Thus, by changing one of the parameters, for example the local atmosphere, and fixing the others, it is possible to study its influence on the formation of new phases and their final physical properties.

The atmosphere of milling is an important factor in the properties of the final product, as has been recently reported by Pochet *et al* (1995). In the case of the metallic Fe powder, it has been shown that the final milled materials are different for distinct milling atmospheres; the milling of metallic Fe under Ar atmosphere for 100 h produces no evidence for the formation of a new phase (Schaaf *et al* 1994), while under N₂ atmosphere the milling of the Fe powder for 264 h

leads to the formation of three phases (Jayasuriya *et al* 1993). On the other hand, it has been reported by Coey (1996) that binary rare earth intermetallic compounds can accommodate small atoms, such as hydrogen, carbon or nitrogen, in interstitial sites of their crystalline structure. Thus, by applying milling procedures to the ErFe_2 intermetallic compound under different atmospheres one can study the stabilization and the formation of new phases that may occur during the milling procedures.

In the present work, XRD and MS results have been combined to detect and to study the new phases and the structural changes that have occurred during the high-energy milling, under two different gases (argon and nitrogen), of the ErFe_2 intermetallic compound and of the chemical elemental powders of Fe and Er with the stoichiometric composition of the compound. The as-prepared ErFe_2 intermetallic compound forms in the C15-type Laves phase and orders magnetically at 596 K (Connolly and Copenhagen 1972).

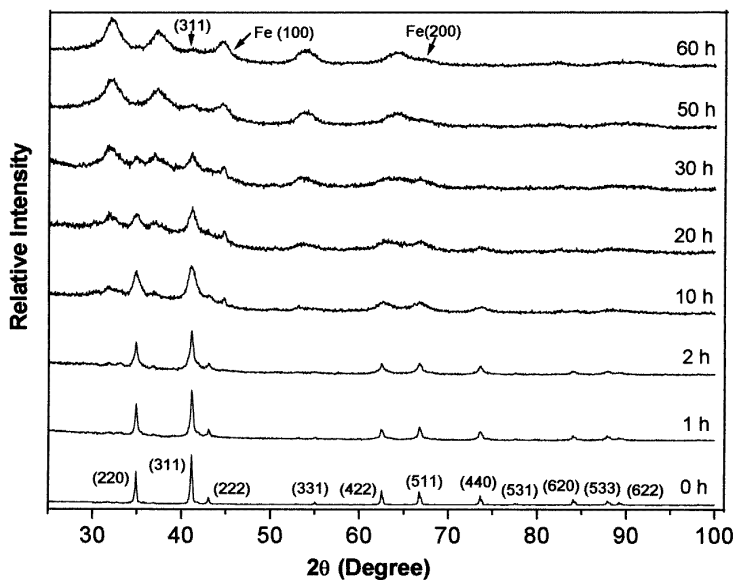
2. Experimental conditions

Two series of four buttons of the ErFe_2 intermetallic compound were prepared by arc melting the high-purity metals under Ar atmosphere. Each button weighted about 3 g and they were heat treated in evacuated quartz tubes for about 120 h at 900 °C. For each series, small pieces that were taken from the buttons were put together and powdered under acetone for x-ray and Mössbauer analysis, in order to check their structural and hyperfine parameters. About 12 g of the compound was then sealed, under high-purity Ar (sample A) or under N_2 (sample B) atmosphere, in a hard steel vial and clamped in a commercial vibrating frame machine. The milling tool used here is a massive cylinder of the same material as the container; the cylinder occupies 57% of the vial internal volume. More details of the milling tools and experimental procedures have been described elsewhere (Larica *et al* 1995). Samples were collected at pre-defined milling times and stored in vacuum for later analysis. The samples were manipulated inside a glove box also under a high-purity Ar atmosphere to prevent oxidation and contamination with other gases.

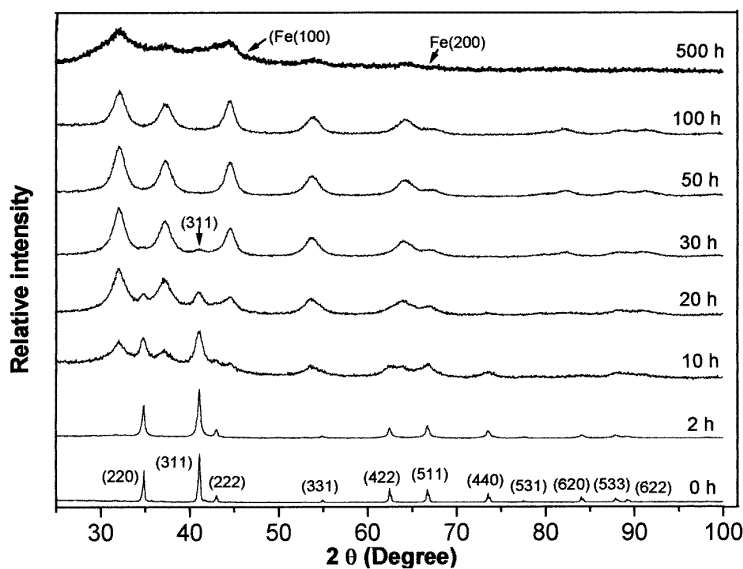
^{57}Fe Mössbauer spectra of all collected samples were measured with a $^{57}\text{Co}:\text{Pd}$ radioactive source in a conventional transmission geometry at room temperature. In the case of sample A with 60 h of milling, the spectrum of the milled material was also taken at 4.2 K with a $^{57}\text{Co}:\text{Rh}$ source, with the source and absorber being kept at the same temperature. The centre shift (CS) values were taken relative to $\alpha\text{-Fe}$ at room temperature (RT). X-ray diffraction patterns (XRD) were obtained from all samples with $\text{Cu K}\alpha$ radiation. AC magnetic susceptibility measurements (χ_{sc}) were performed using a home made system with the in- and out-of-phase induced emf voltage read by a lock-in amplifier; a 1.0 G probe field amplitude and an AC field frequency of 500 Hz were applied. The sample temperature could be varied from 77 K to 300 K. Final compositions have been checked by energy dispersive x-ray spectroscopy (EDS) analysis. The EDS analysis of sample A milled for 100 h gave roughly a similar Fe content as the initial compound, within the EDS accuracy. However, the EDS analysis of the sample B for milling times longer than 500 h shows a contamination of Cr (2 at.%) due to the vial tools, leading us to stop the milling process.

3. Results and discussion

Figures 1(a) and (b) show the x-ray diffraction patterns for several milling times of the ErFe_2 intermetallic compound milled under Ar and N_2 atmospheres, designated as samples A and B, respectively.



(a)



(b)

Figure 1. (a) and (b) x-ray diffraction patterns as a function of milling time of the ErFe_2 compound milled under Ar and N_2 atmospheres, respectively.

For the as-prepared compound, the diffraction pattern shows just the Bragg peaks in accord with the known cubic structure of the ErFe_2 compound, as indicated by the Miller index. In both samples A and B, with increase of milling time the intensities of these diffraction lines decrease and their line widths become broader, indicating a reduction of the grain sizes and an initial process of structural disordering.

In the case of sample A with 60 h of milling (see figure 1(a)), only a weak broad peak associated with the [311] Bragg reflection of the initial compound remains in the x-ray pattern, leading us to conclude that long-range ordering of the compound has been lost. As will be shown below, Mössbauer results indicate the formation of an amorphous phase. In addition, broad diffraction lines appear above 10 h of milling indicating the formation of other new crystalline phases. One set of these new Bragg peaks has been well matched with those of metallic iron, i.e., at angle values (2θ) about 44.7, 65.1 and 82.4°, corresponding to a bcc structure with a lattice parameter of 2.87 Å. A second set of Bragg peaks, with 2θ values at about 32.5, 37.2 and 53.8°, is fitted with an fcc Er crystalline structure having a lattice parameter of 4.84 Å. More details about this fcc Er phase will be discussed below.

Similar features on the diffraction patterns have been observed, in the case of sample B (see figure 1(b)), for intermediate milling times ($2 < t_m < 100$ h), i.e., the sample also shows the presence of the new phases as observed in sample A. With 50 h of milling, the Bragg reflection peaks associated with the initial compound are no longer observed in the x-ray patterns, but only those Bragg peaks of the two new crystalline phases mentioned above, indicating that the chemical elements of the compound were mostly segregated. From the XRD results of samples A and B it can be preliminarily concluded that the milling of the ErFe₂ compound produces segregation of the elements, yielding nanocrystallites of metallic Fe and fcc Er phase. The segregation effect seems to occur earlier under N₂ than under Ar atmosphere. This result will be supported by Mössbauer results in the next section.

Concerning the fcc Er phase observed in the XRD results of the milled samples A and B, Alonso *et al* (1991, 1992) have reported that the milling of rare-earth (RE) metals can lead to a high-pressure fcc RE structure stabilized by oxygen and nitrogen impurities, since such gases are present during the milling process. Thus, by combining the XRD results of samples A and B, two reasons indicate that the fcc Er phase was stabilized by nitrogen: the known fcc ErN phase (Klemm 1956) has a lattice parameter similar to that found in the present experiments and, in addition, the milling of sample B has been performed under a rich N₂ atmosphere inducing an earlier formation of ErN phase compared with sample A, and subsequent segregation of the chemical elements. Therefore, the possible occurrence of an ErN phase in the case of ErFe₂ compound milled under Ar may be possibly due to a residual gas contamination that may have occurred during the several sample manipulations performed inside the glove box. The formation of the fcc phase in pure rare earth has also been detected after milling under Ar, due to N₂ contamination, as reported by Alonso *et al* (1991, 1992).

For the case of sample B, Bragg peaks of the α -Fe and ErN phases are superimposed on a broad background, which seems to develop at the expense of the two crystalline phases as noted in the XRD pattern for the 500 h sample in figure 1(b). This new phase may only have a short-range order and it will be discussed below with the Mössbauer spectra results.

Figure 2 shows the room-temperature ⁵⁷Fe Mössbauer spectra of the samples obtained from the ErFe₂ compound milled under Ar atmosphere for indicated times. The zero hour Mössbauer spectrum displays two magnetic crystalline components (sites 1 and 2), which were fitted with the usual hyperfine parameters of this phase reported by Guimarães (1971). Therefore, by combining XRD and MS results of the zero hour sample we conclude that the initial sample presents a single phase, i.e. the expected C15 Laves phase of the ErFe₂ intermetallic compound. However, as the milling time increases a doublet and a sextet appear in the Mössbauer spectra. The magnetic component, as is clear at 10 h of milling, was fitted with a CS value similar to that of metallic Fe, a broad line width ($\Gamma = 0.48(2)$ mm s⁻¹) and a magnetic hyperfine field (B_{hf}) of 32.2(2) T. Thus, XRD and MS results give us strong support to attribute this phase to segregated Fe atoms, forming nanocrystallites of metallic Fe.

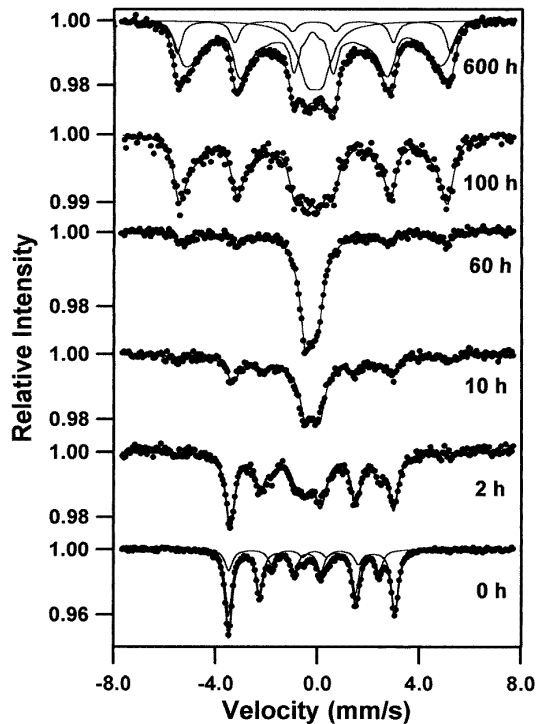


Figure 2. ^{57}Fe Mössbauer spectra at 300 K versus milling time, of the ErFe_2 compound milled under Ar atmosphere. The full line represents the fitting result.

The observed doublet that is present in the spectra of the milled samples was fitted with an electric quadrupole distribution, having average values of $CS = -0.14(3) \text{ mm s}^{-1}$ and $QS = 0.44(2) \text{ mm s}^{-1}$. The hyperfine parameter values are close to those reported by Ghafari *et al* (1994) for amorphous ErFe_2 phase obtained in films. The relative area of this doublet increases at the expense of the initial spectrum components and reaches the maximum value of 88% at 50 h of milling. For longer milling times no contribution of the initial compound was observed in the Mössbauer spectra (see figure 2). For milling times longer than 100 h, the Mössbauer spectra are analysed with three components: the doublet, with 22% of relative area at 100 h, and two magnetic components. The magnetic components are associated with the metallic Fe, since the component has similar hyperfine parameters, and to a rich Fe disordered phase alloy having $\langle B_{hf} \rangle$ of 25.0 T, and it is forming at the expense of recombination of the phases.

The observed doublet is associated with an amorphous Er/Fe alloy with a composition close to that of the initial compound, as will also be supported by Mössbauer and susceptibility measurements at low temperatures discussed below.

Figure 3 shows the relative area of the Mössbauer subspectra versus milling time observed in sample A. From 1 to 60 h of milling, the relative area of the doublet increases faster than the magnetic component associated with metallic Fe, indicating that the formation of the Er/Fe amorphous alloy is mainly a result of two competing processes: the formation and homogenization of an amorphous phase on one hand and the chemical segregation of the alloy components on the other. The instability of the amorphous phase due to its relatively high enthalpy (Schultz 1988) is consistent with the observed subsequent segregation process. With

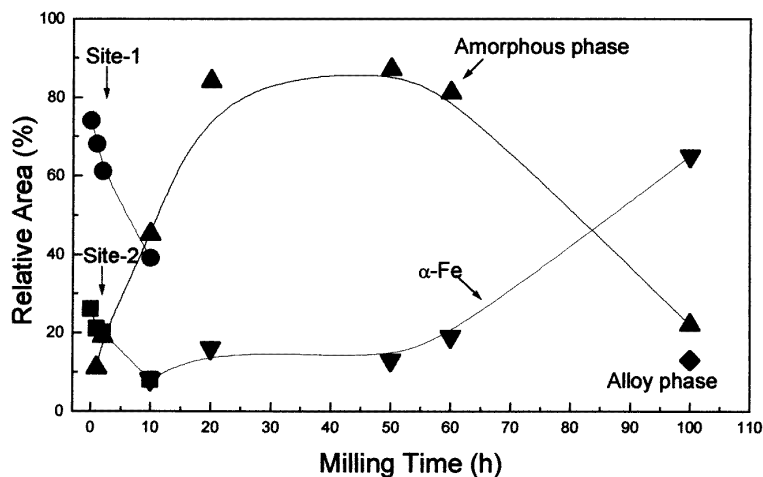


Figure 3. Behaviour of relative area versus milling time of the Mössbauer subspectra observed in the ErFe_2 compound milled under Ar atmosphere. The lines that connect the experimental points are only a guide to the eyes.

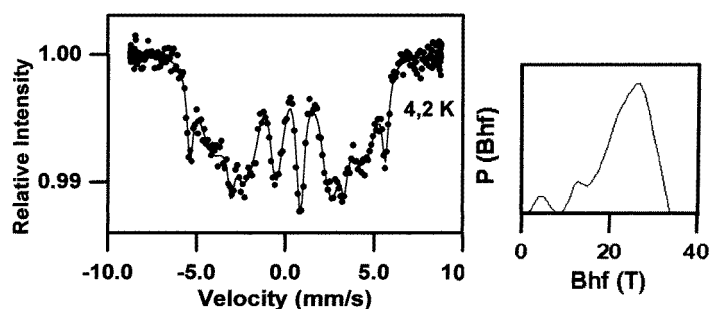


Figure 4. ^{57}Fe Mössbauer spectrum of the 60 h milled ErFe_2 compound obtained at 4.2 K. The full line represents the fitting result. The curve on the right-hand side is the distribution of magnetic hyperfine fields.

100 h of milling, the Mössbauer spectrum is basically composed by the magnetic components, where the metallic Fe component has 65% of relative area. The segregation effect in an amorphous phase obtained by milling YFe_2 compound has been recently reported by Larica *et al* (1998). Above 100 h, a disordered alloy is formed at cost of metallic Fe and the doublet components. With 600 h, the phase associated to a disordered alloy has 62% of Mössbauer relative area.

Figure 4 shows the Mössbauer spectrum of sample A milled for 60 h and measured at 4.2 K. It can be seen from the spectrum that it is composed of two magnetic components: a very broad magnetic field distribution and a crystalline magnetic component. The magnetic hyperfine field distribution curve, plotted on the right-hand side of figure 4, corresponds to the result of fitting the broad magnetic field component.

The crystalline sextet already mentioned is associated with metallic Fe and it has a $B_{hf} = 34.5(3)$ T, at 4.2 K. The observed magnetic hyperfine field distribution is associated with the room-temperature doublet now magnetically ordered. This distribution has an average magnetic hyperfine field ($\langle B_{hf} \rangle$) of about 23.0(9) T and a most probable field value of 26.0 T, as

clearly shown in the right-hand side of figure 4. The $\langle B_{hf} \rangle$ value fits in the tendency of magnetic hyperfine field at 4.2 K for amorphous rare-earth-Fe reported by Heiman *et al* (1976). The AC magnetic susceptibility (χ_{AC}) versus temperature of sample A, milled for 60 h, is shown in figure 5. It presents a broad transition peak at about 190 K, which fits with the behaviour of the magnetic transition temperatures for amorphous rare-earth- Fe_2 phases (Heiman *et al* 1976). Therefore, by combining the Mössbauer and χ_{AC} results it can be concluded that the doublet, observed at 300 K in the milled samples, is due to an amorphous phase of ErFe_2 .

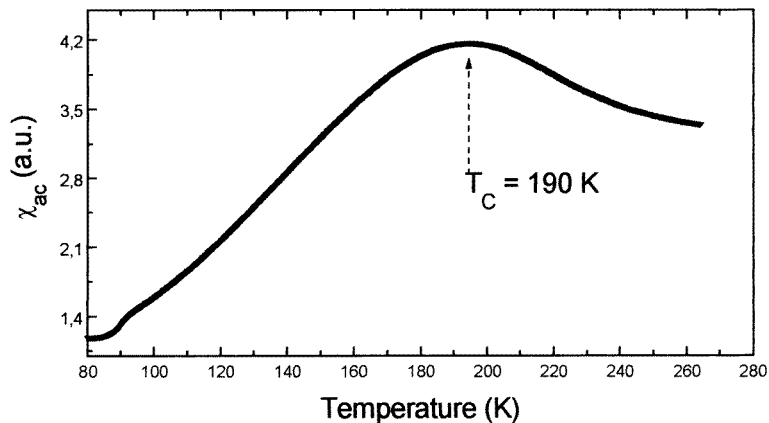


Figure 5. AC magnetic susceptibility versus temperature of the 60 h milled ErFe_2 compound under Ar atmosphere.

Figure 6 shows the ^{57}Fe Mössbauer spectra obtained at 300 K for different milling times of the ErFe_2 compound milled under N_2 atmosphere. For this series, the zero hour Mössbauer spectrum displays, as expected, two magnetic crystalline components (sites 1 and 2), which were fitted with the usual hyperfine parameters of the C15 Laves phase (Guimarães 1971).

Therefore, the XRD and MS results indicate that the initial sample is a single phase. With increase of the milling time, up to 2 h of milling, the Mössbauer spectra display a doublet with the same hyperfine parameters as the doublet obtained in sample A. Therefore, this doublet is also attributed to the amorphous ErFe_2 phase, and it has its maximum relative area of about 56% with 20 h of milling, while, in the case of Ar atmosphere, it shows 88% of maximum Mössbauer relative area with 50 h of milling. Milling times above 2 h, in sample B, also lead to the appearance of a sextet, similar to that already observed in sample A, which is associated with metallic Fe probably with some Er impurities trapped in it. The relative area of this broad sextet increases at the expense of the doublet and of the magnetic components of the initial compound. Its relative area reaches the maximum value of 50% at about 50 h of milling.

Starting at 30 h of milling, a phase formed by Er and N atoms in metallic Fe shows up in the Mössbauer spectra (see the distribution curve in figure 6) and it was fitted with a magnetic hyperfine field distribution. The adoption of this model is based on the different $\text{CS} = +0.10 \text{ mm s}^{-1}$ and $B_{hf} = 31.5 \text{ T}$ values, when they are compared with those associated with the metallic Fe phase. However, with the increase of the milling time a more homogeneous Fe-Er-N alloy is formed due to the increasing atomic diffusion of the atoms. The Mössbauer spectrum of sample B milled at 500 h still shows the presence of two phases: one associated with the metallic Fe rich phase that persists from the initial segregation process, and a second one with a broad magnetic distribution attributed to an Fe-Er-N disordered alloy. Thus, by combining the XRD and MS results it can be said that the final milled material of sample B

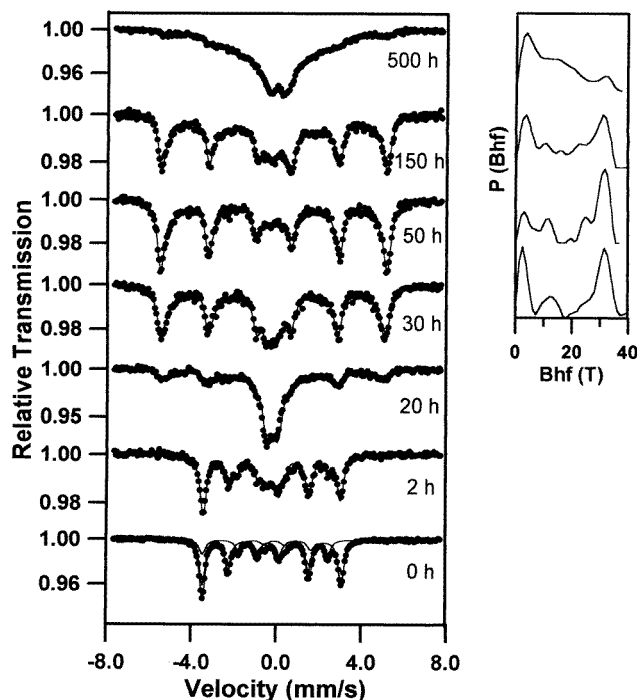


Figure 6. ^{57}Fe Mössbauer spectra at 300 K versus milling time of the ErFe_2 compound milled in N_2 atmosphere. The full lines represent the fitting result. The curves on the right-hand side are the distribution of magnetic hyperfine fields.

has basically three phases: ErN , metallic Fe and Fe-Er-N . XRD and MS results also lead us to conclude that two of these phases, ErN and metallic Fe , contribute in small amounts to the total volume of the final material. The dominant phase in the 500 h milled powder, the Fe-Er-N disordered alloy, has a magnetic ordering temperature not far above room temperature, as suggested by the Mössbauer spectrum (500 h) shown in figure 6. This observation indicates that the Fe-Er-N disordered alloy has ordering temperature higher than the ErFe_2 amorphous alloy.

In order to understand the influence of atmosphere on the amorphization process of the ErFe_2 phase, a new sample (C) was prepared from milling the mixture of Er and Fe elemental powders, under N_2 local atmosphere, with the ErFe_2 composition. Figure 7 displays the Mössbauer spectra of sample C obtained at 300 K for different milling times. The zero hour Mössbauer spectrum, not shown here, is composed only by the lines of metallic Fe . With increase of the milling time, the contribution of metallic Fe to the spectra is reduced due to the formation of a paramagnetic component. For example, with 42 h of milling the Mössbauer spectrum displays two phases: one fitted with hyperfine parameters of metallic Fe and therefore attributed to Fe powder not yet combined with Er , and a second phase fitted with an electric quadrupole distribution, which has the hyperfine parameters of the ErFe_2 amorphous phase found in the samples A and B, and therefore is associated with the ErFe_2 amorphous phase.

The behaviour of the relative area of the Mössbauer subspectra versus milling time is shown in figure 8. The maximum relative area of the ErFe_2 amorphous phase occurs between 49 and 68 h of milling and reaches about 87% of the total area of the spectrum. However, for 94 h of milling the contribution of the metallic Fe phase increases to about 40%, indicating that longer milling procedures have induced a segregation process in the amorphous phase.

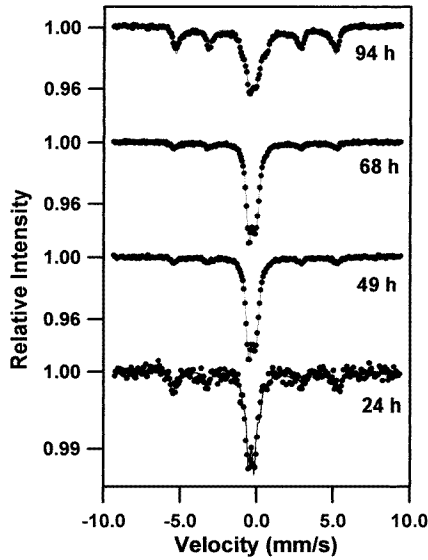


Figure 7. ^{57}Fe Mössbauer spectra at 300 K versus milling time obtained from milling the chemical elemental powders of Er and Fe, at stoichiometric composition of ErFe_2 phase, under N_2 atmosphere.

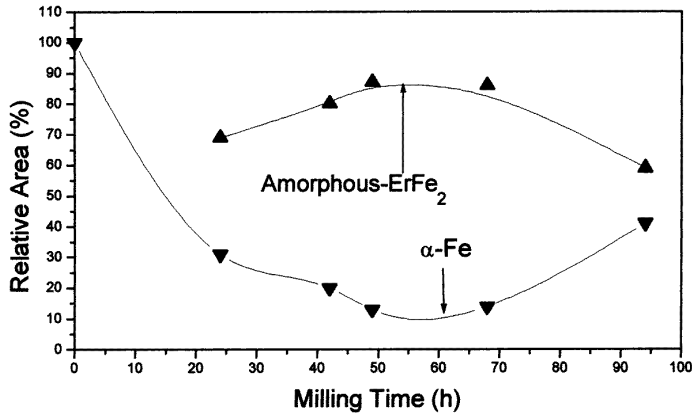


Figure 8. Behaviour of relative area versus milling time of the Mössbauer subspectra observed in the milled Er and Fe powder with ErFe_2 composition, under N_2 atmosphere. The lines that connect the experimental points are only a guide to the eyes.

4. Conclusions

Different metastable phases have been detected by milling ErFe_2 intermetallic compound under two different atmospheres, Ar and N_2 . Milling the compound under Ar atmosphere basically leads the ordered crystalline compound to a topologically disordered phase, i.e. an amorphous ErFe_2 phase. The milling results of the intermetallic compound under N_2 atmosphere indicate that nitrogen atoms cannot be accommodated at the compound interstitial sites, because the compound phase loses its chemical stability and gives a chemical segregation process of the elements. It can also be concluded that the segregation effect is faster than the amorphization

process in the case of ErFe_2 compound milled under N_2 , in contrast to the Ar case. The ErFe_2 amorphous phase has been detected in both local milling atmospheres; however the amorphization process is more effective under Ar atmosphere.

The milling of chemical elemental powders of Fe and Er at the stoichiometric composition of ErFe_2 leads to an amorphous phase, and no evidence of chemical segregation has been observed up to 68 h of milling. The segregation has been detected only after the formation of the amorphous phase. Thus, the segregation effect that has been observed in samples A and B seems to result from two different processes: in the case of Ar atmosphere the segregation appears after the complete amorphization of the compound, while in the N_2 case the segregation process may be induced by the presence of nitrogen atoms going into the crystalline structure of the compound, prior to the amorphization. The segregation process forms basically two phases: metallic Fe probably with Er impurities and ErN. These two phases may recombine after longer milling time (500 h), and a new disordered Fe–Er–N phase is formed in the final milled material.

Summarizing, it is important to emphasize two aspects: (1) an amorphous phase can be obtained by milling the ErFe_2 compound, without larger segregation of the chemical elements, if the milling procedures are performed under an inert (Ar) atmosphere and no contamination from residual gases, like oxygen and nitrogen, is present during the milling procedure, (2) the ErFe_2 amorphous phase can be obtained by milling a mixture of Fe and Er powder with ErFe_2 composition under any atmosphere.

Acknowledgments

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