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# Structural and magnetic properties of grain boundaries in Fe<sub>60</sub>Cr<sub>40</sub> alloy synthesized by mechanical alloying

A Fnidiki<sup>1</sup>, C Lemoine and J Teillet

Groupe de Physique des Matériaux UMR CNRS 6634, 76821, Mont-Saint-Aignan Cédex, France

E-mail: abdeslem.fnidiki@univ-rouen.fr

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## Abstract

Mechanical alloying of iron and chromium powder mixtures was performed from 0 to 190 h milling times. X-ray diffraction, Mössbauer spectrometry and differential scanning calorimetry were used to determine the structural and magnetic properties of the intergranular zone, which was associated with a very disordered grain boundary structure, paramagnetic at 300 K. This structure is assumed to be due to the presence of oxygen and nitrogen atoms, forming a mixture of amorphous FeCr + O + N alloy. Between 21 and 85 h, the hyperfine parameters of the magnetic contribution, and therefore the properties of the Fe<sub>60</sub>Cr<sub>40</sub> nanograin cores, are constant, but the paramagnetic fraction associated with the intergranular zone increases. At 85 h, the paramagnetic contribution represents 100% of the Mössbauer spectrum.

Moreover, after very long milling times, we have evidenced a de-mixing reaction which results in preferential oxidation and nitrogenation within the very disordered structure.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Mechanical alloying (MA) is a dry and high-energy milling process, which has attracted considerable interest in recent years owing to the wide range of materials, often with non-equilibrium structures, which can be synthesized [1–7]. The end product depends on many parameters such as the milling conditions [8–12] and the thermodynamic properties of the milled system.

<sup>1</sup> Author to whom any correspondence should be addressed.

Structural and magnetic properties of  $\text{Fe}_{100-x}\text{Cr}_x$  obtained by MA are described in review papers [13–19]. Recently, MA under gas atmosphere has been reported to produce an amorphous phase [20–23] or some crystalline compounds [24] through the solid–gas reaction.

We have shown [25] that MA of  $\text{Fe}_{1-x}\text{Cr}_x$  powder mixtures (for  $x \leq 40$  at.%) gives particles of several micrometres consisting of nanocrystalline grains with grain sizes of about 10 nm. After 30 h of milling, a so-called stationary mixing state is obtained and the powder is an alloy at the atomic scale. From Mössbauer experiments, the analysis of the hyperfine field distributions has shown that the nanograin cores are (for  $x \leq 40$  at.%) quite homogeneous in composition and have hyperfine parameters close to those of the bulk crystalline alloys with the same composition.

In a following work [26], effects of oxygen and nitrogen on the properties of FeCr powders elaborated by MA were evidenced. Our results agree with the fact that during MA the oxygen and nitrogen are absorbed in the grains of the powder and contribute to create a very disordered Fe–Cr + O + N grain boundary structure, paramagnetic at 300 K. These results show that a detailed study of the properties of a nanostructured powder elaborated by MA needs to take carefully into account the influence of residual gases.

In this work, we are going to characterize in more detail the intergranular zone.

## 2. Experiment

MA of a mixture of pure Cr powder (99.0%) and pure Fe powder (99.9%) was carried out in a Fritsch planetary mill ('Pulverisette P5'), using hardened commercial (C) Fritsch steel vials of 80 cm<sup>3</sup> and five balls of diameter 20 mm. The weight of the initial mixed powder sample for  $\text{Fe}_{60}\text{Cr}_{40}$  was about 12 g and the ball to powder weight ratio was 13:1. To minimize oxidation, the vials were always sealed under argon atmosphere.

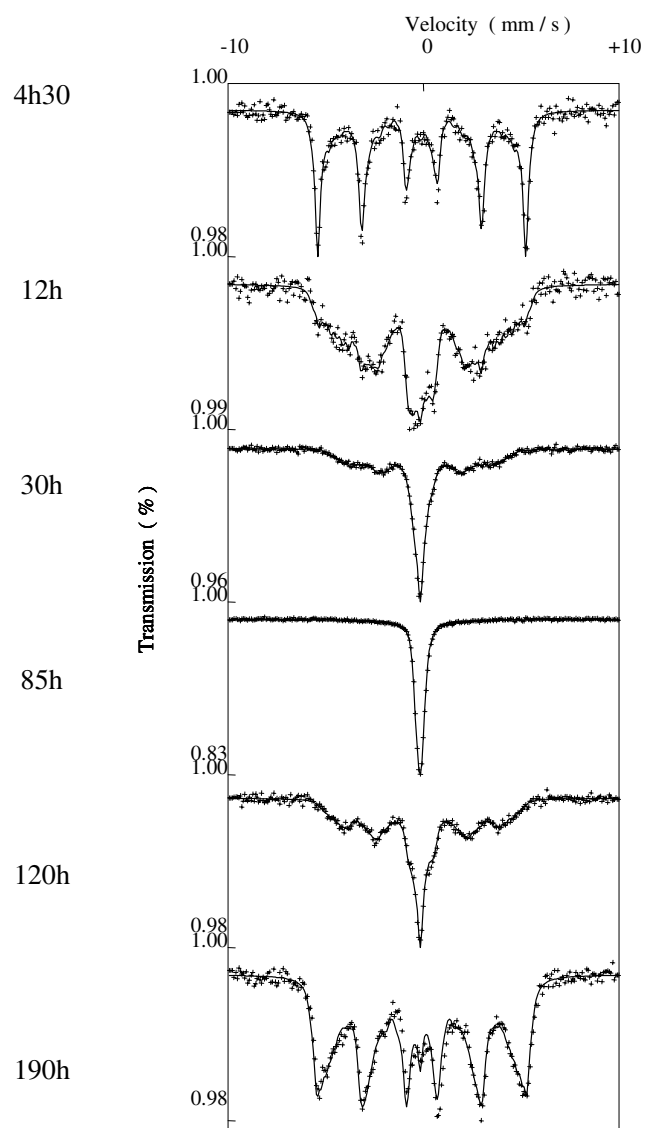
The milled powders were analysed by x-ray diffraction (XRD) and Mössbauer spectrometry, before and after thermal treatments. XRD measurements, carried out on a Siemens powder diffractometer using Co K $\alpha$  radiation ( $\lambda = 0.1789$  nm), allowed the average grain size to be roughly estimated by the Scherrer method. As the lattice parameters of Fe and Cr are very similar, the diffraction peaks overlap and the result gives only an average result on Fe, Cr and FeCr coherent domains.

Mössbauer spectra were recorded in transmission geometry at room temperature using a <sup>57</sup>Co source in a rhodium matrix. The Mössbauer spectra were fitted with a least-squares technique using the histogram method related to a discrete distribution. A correlation between the hyperfine field ( $B_{hf}$ ) and the isomer shift (IS) was used to take into account the environment distributions. The IS at the <sup>57</sup>Fe nuclei is given relative to  $\alpha$ -Fe at room temperature.

Thermal treatments were performed under an inert atmosphere of argon by differential scanning calorimetry (SETARAM Labsys<sup>TM</sup> TG-DSC8), with different heating rates from 5 to 20 K min<sup>-1</sup>.

## 3. Mössbauer results from 0 to 190 h of milling

Room-temperature Mössbauer spectra of powder mixtures after different milling times in commercial vials are reported in figure 1. From 12 h of milling, one observes, in addition to the expected magnetic contribution of  $\text{Fe}_{60}\text{Cr}_{40}$  crystalline alloy, a paramagnetic contribution whose fraction increases with the milling time. With the milling time, three stages can be distinguished.

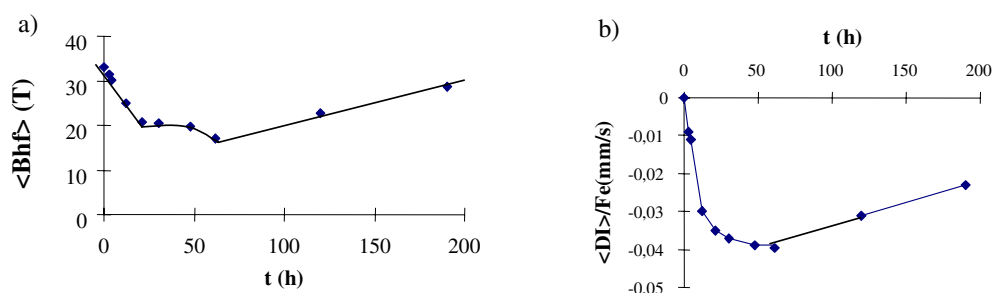


**Figure 1.** Mössbauer spectra of Fe<sub>60</sub>Cr<sub>40</sub> powder mixture after different milling times at 300 tr min<sup>-1</sup> in commercial vials.

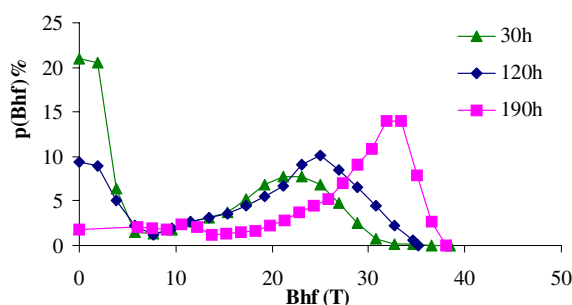
### 3.1. Stage of mixing from 0 to 20 h

From 0 to 20 h we observe two contributions.

- A magnetic contribution [25] attributed to the nanograin core, whose hyperfine parameters evolve until the stationary mixing state. At this stationary mixing state, reached after approximately 20 h, the hyperfine parameters remain constant and are close to these of Fe<sub>60</sub>Cr<sub>40</sub> bulk crystalline alloys, so the nanograin cores have the composition of the initial powder mixture.
- A paramagnetic contribution that will be studied in more detail in the next paragraphs.



**Figure 2.** (a)  $\langle B_{hf} \rangle$ , (b)  $\langle IS \rangle$  of magnetic contributions of the mixture.



**Figure 3.** Hyperfine field distributions versus the milling time corresponding to the plotted spectra in figure 1.

### 3.2. Stage of topological disorder from 21 to 85 h

Between 21 and 85 h, the hyperfine parameters of the magnetic contribution, and therefore the properties of nanograins, are constant, but the paramagnetic fraction increases. At 85 h, the paramagnetic contribution represents 100% of the Mössbauer spectrum. As the grain composition (in FeCr) is constant, the paramagnetic contribution cannot be attributed to the chemical fluctuations, but has to be associated with structural changes.

### 3.3. Stage of de-mixing from 85 h

From 85 to 190 h, the Mössbauer paramagnetic fraction decreases and a new magnetic contribution increases. This magnetic contribution has different properties with respect to that obtained at the mixing stage. The mean hyperfine field of this contribution increases with the milling time, from 20.4 T at 30 h to 22.7 T at 120 h and 28.7 T after 190 h (figure 2(a)). Similarly, the IS increases after 85 h of milling (figure 2(b)). In addition, the shape of hyperfine field distributions (of contributions corresponding to a field  $> 10$  T) changes. At 30 h the distribution is binomial with a maximum around 20.5 T, while for the long milling times it is no longer binomial, narrowed and centred on 33 T (figure 3).

All these results ( $IS \rightarrow 0 \text{ mm s}^{-1}$  and  $B_{hf} \rightarrow 33 \text{ T}$ ) show that the environment of grain atoms is strongly modified by the long milling times. The values of hyperfine parameters, as well as the change of hyperfine field distributions versus the milling times, reveal a progressive enrichment in iron of the iron atom environment. The observed phenomenon is like a de-mixing of the FeCr solid solution.

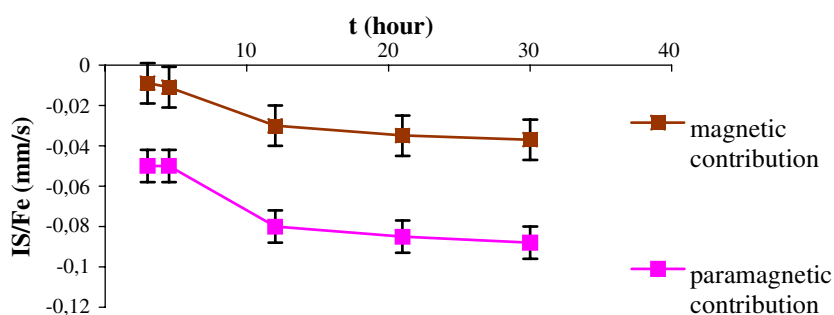


Figure 4. IS of magnetic and paramagnetic contributions versus the milling time.

#### 4. Nature of the very disordered state associated with the intergranular zone

As recalled in the introduction, we have shown that the grain boundaries are disordered, probably by the presence of oxygen and nitrogen, and that the intergranular zone will continuously enlarge with the milling time, globally keeping the same composition and the same properties [26]. This intergranular zone corresponds to a paramagnetic Mössbauer spectrum, and can represent 100% of the Mössbauer spectrum after 85 h of milling.

The exact structure of this disordered zone obtained by MA is difficult to elucidate. The XRD is not usable for the long milling times, because the intensity of peaks becomes too weak. Some TEM analyses that we performed on the powder milled at 85 h show zones with crystallites, in some rare particles of powder. This indicates that the paramagnetic ‘phase’ still presents some crystallized areas. Nevertheless the low amount of crystalline zone seems to indicate that the remaining material is amorphous. These results agree with previous studies by high-resolution electronic microscopy [27], to characterize the structure of milled FeCr powder under atmosphere of nitrogen.

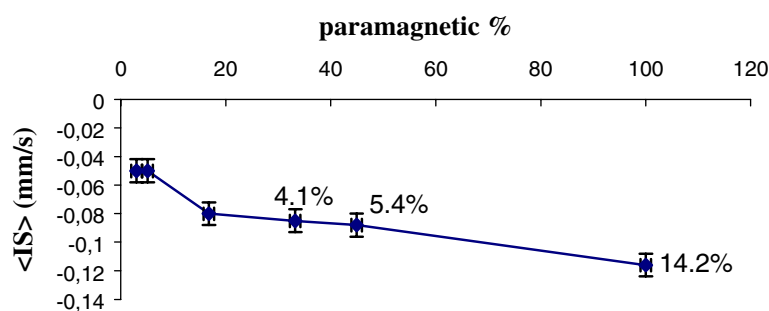
Consequently, the paramagnetic contribution obtained by MA agrees with a topologically disordered structure, but one cannot exclude that there subsists a crystalline order at short distance (approximately on 1–2 nm) in some particles of powder.

##### 4.1. Isomer shift results

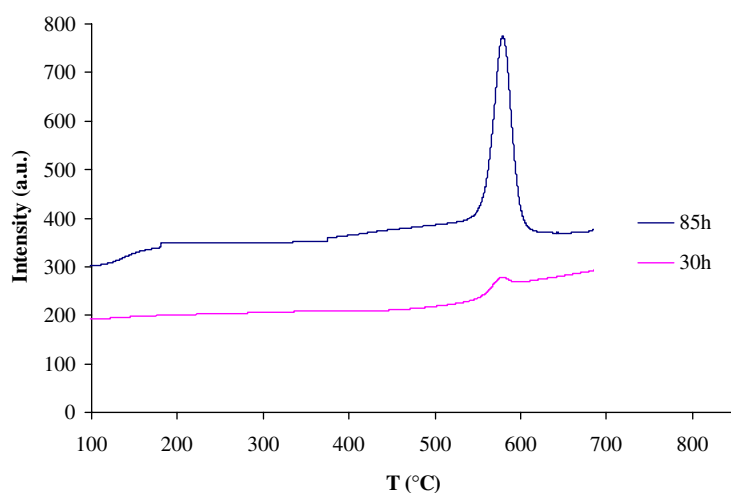
**4.1.1. Variation with the milling time.** Mössbauer spectra have been adjusted taking into account a paramagnetic contribution (intergranular zone) and a hyperfine field distribution (grain core). For the first hour of milling, the IS of the paramagnetic contribution decreases when the milling time increases (figure 4). This concerns the stage of mixing between the iron and the chromium. In the intergranular zone, as in the case of the grain cores, to change an iron atom for a chromium atom in the vicinity of the iron contributes to decreasing the IS. However, the IS of the intergranular zone is always less than that of the grain core (figure 4). This is due to the very disordered structure of the intergranular zone. Indeed, in the case of an amorphous FeCr structure, the coordination number increases as compared with that of the crystal as well as the hybridization of 3d layers, thus increasing the effect of the Cr on the IS [28].

**4.1.2. Variation with the paramagnetic fraction.** The IS variation versus the Mössbauer paramagnetic fraction  $F_p$  is reported in figure 5. One distinguishes three areas.

- From 0 to 20% the IS decreases. This is the step of mixing between chromium and iron.



**Figure 5.**  $\langle IS \rangle$  of the paramagnetic contribution versus the paramagnetic fraction  $F_p$ . Percentages reported on the curve correspond to the measured content of (O + N) (% mass).



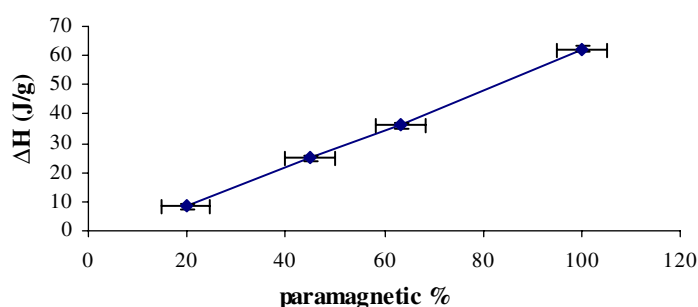
**Figure 6.** DSC curves of mixture after different milling times in the commercial vials.

- From 20 to 45%, IS remains nearly constant, indicating that the local order does not change. Nevertheless, the content in light atoms increases. Thus, the local order in the intergranular zone remains constant but its thickness should increase.
- When the paramagnetic contribution  $F_p$  occupies more than 50% of the total volume, the IS decreases again. Consequently, the local order in the intergranular zone is modified. For this value, the total incorporated quantity of oxygen and nitrogen is 14% mass. This effect is probably due to a de-mixing phenomenon. During this de-mixing, iron is surrounded preferentially by iron and the charge density at the iron nucleus increases, leading to the diminution of the IS.

#### 4.2. DSC results

The DSC curves of powder mixtures after different milling times are drawn in figure 6. An exothermic peak is observed at 577 °C on each curve.

The enthalpy ( $\Delta H = \text{peak area}$ ) depends on the milling time (table 1) and linearly increases with the Mössbauer paramagnetic fraction (figure 7). Consequently, the observed



**Figure 7.** Percentage paramagnetic versus  $\Delta H$ .

**Table 1.** Mössbauer percentage and measured enthalpy (by the exothermic peak area), obtained on a milled Fe<sub>60</sub>Cr<sub>40</sub> powder mixture.

	Time (h)	$T_{\max}$ (°C)	% para	$\Delta H$ (J g <sup>-1</sup> )
Commercial vial	30	576	44.9	-24.8
Commercial vial	62	576	70.8	-36.2
Commercial vial	85	579	100	-62.4

Mössbauer paramagnetic contribution has to be associated with the exothermic phenomenon observed in DSC.

#### 4.3. Effects of annealing

Annealings for 5 h at different temperatures have been performed on the powder mixture milled for 30 h in commercial vials. Mössbauer spectra show that the paramagnetic contribution totally disappeared after annealing at 560 °C (figure 8), in agreement with DSC results.

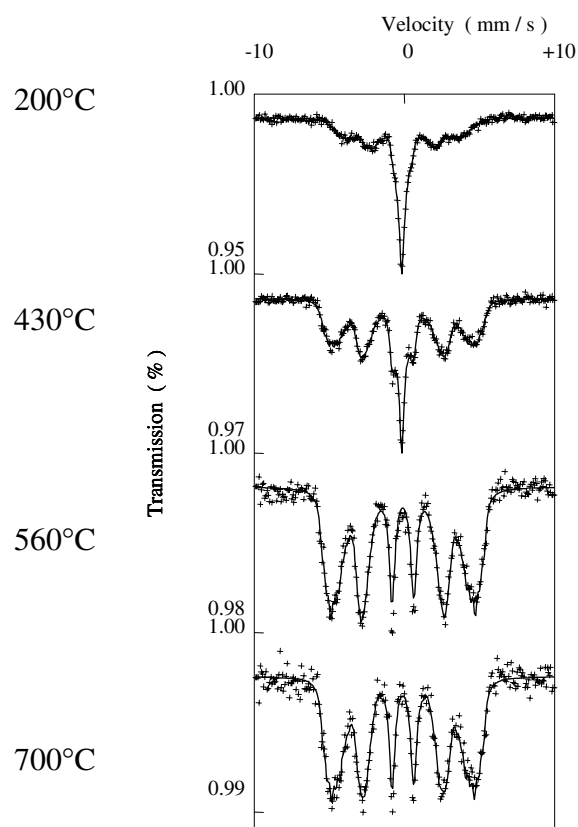
Whatever the annealing temperature, the hyperfine field distributions are characteristic of a solid solution (figure 9). Nevertheless, the mean hyperfine field of distributions increases, from 20.4 T before annealing, to 28 T after annealing at 700 °C. This increase is due to a beginning of the decomposition of the solid solution in a domain rich in Cr and rich in Fe, in agreement with the FeCr phase diagram.

Figure 10 shows the evolution of the grain size, the mean hyperfine field of the magnetic contribution and the Mössbauer paramagnetic fraction versus the annealing temperature.

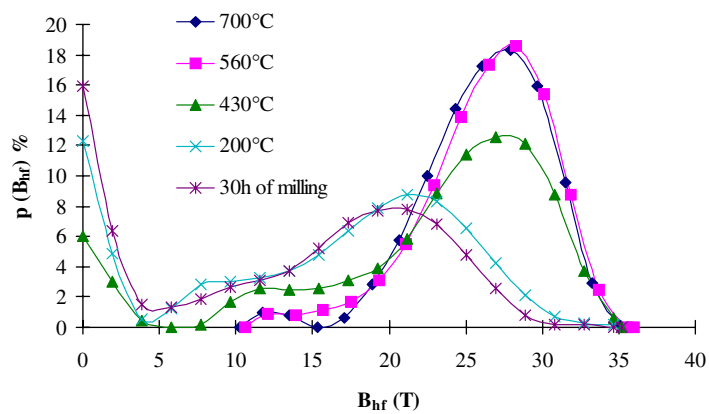
- Below 430 °C, the grain size increases slightly, the mean hyperfine field increases and the paramagnetic fraction almost linearly decreases. This part is assumed to correspond to the ordering of the grain boundaries.
- Above 430 °C, the hyperfine field is nearly constant, so the chemical order in the nanograins is the same as that obtained at 430 °C. The hyperfine field distributions are characteristic of a solid solution (figure 9). In addition, the grain size rapidly increases and the paramagnetic contribution completely disappears. Providing energy by heating has therefore led to the complete crystallization of the intergranular zone.

The XRD patterns confirm that a total crystallization takes place after the annealing at 700 °C (figure 11). Diffraction peaks associated with the FeCr solution are observed, as are some poorly resolved weak peaks. These last peaks have been also observed by other authors [29] during the annealing of milled FeCr powder mixtures, and have been attributed to a phase rich in chromium, resulting from the decomposition of the solid solution. We attribute



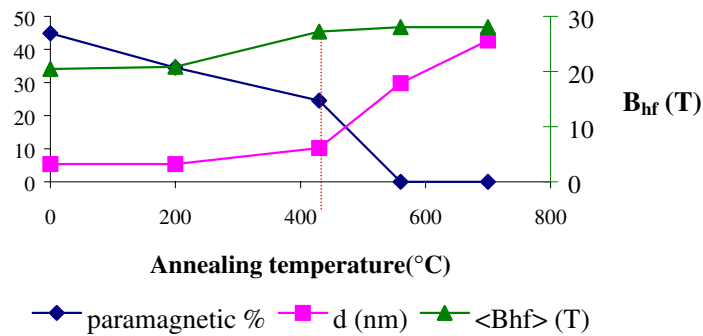


**Figure 8.** Mössbauer spectra at 30 h of milling time, after annealing at 5 h to indicated temperatures.

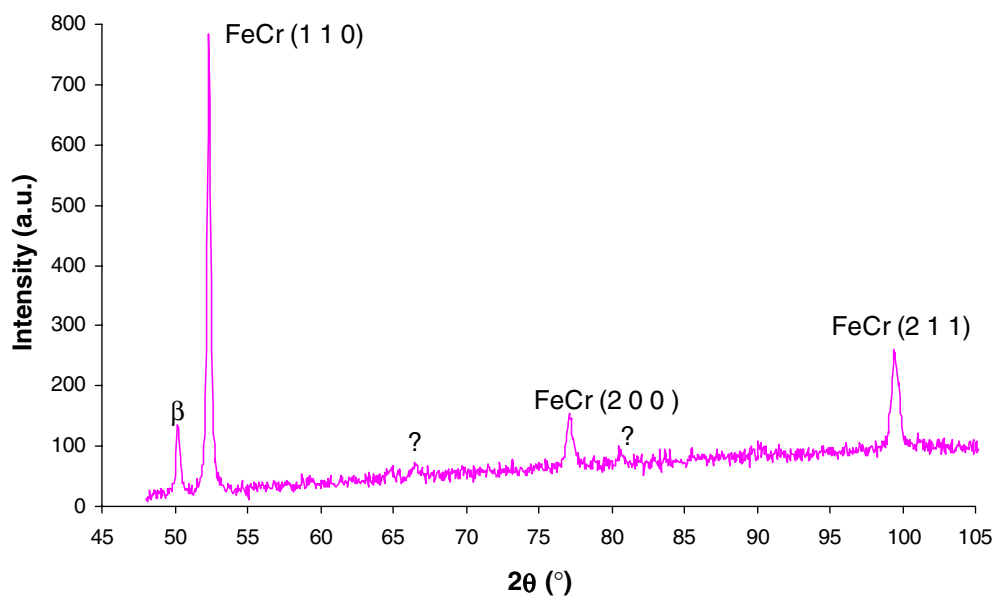


**Figure 9.** Hyperfine field distributions of spectra plotted in figure 8.

these peaks to the  $\beta$ -Cr<sub>2</sub>N phase, but the poor statistics and the few peaks associated with this phase do not allow us to conclude definitively. In addition, some peaks could be attributed to poorly crystallized oxides.



**Figure 10.** Mössbauer paramagnetic fraction, grain size and mean hyperfine field of magnetic contributions versus the annealing temperature (5 h).



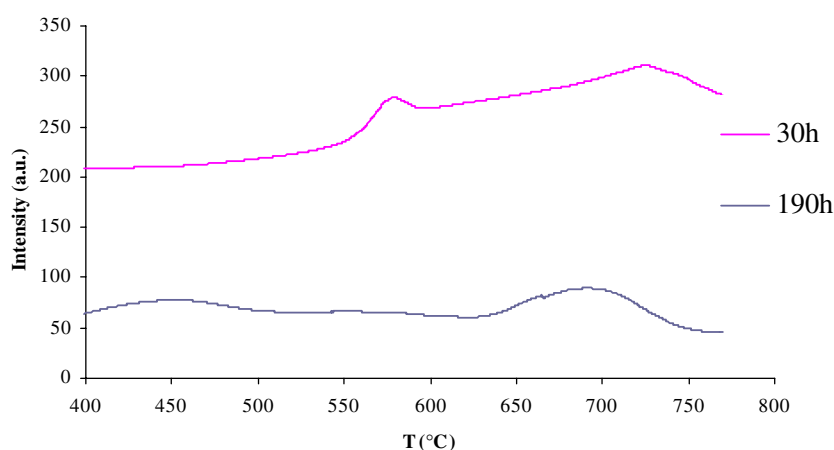
**Figure 11.** XRD patterns at 30 h of milling time and annealing for 5 h at 700 °C.

These results indicate that the zone very disordered by oxygen and nitrogen crystallizes at 580 °C. This crystallization is accompanied by the precipitation of nitrides or by phases very rich in chromium, containing oxygen.

### 5. De-mixing mechanism

An extended milling beyond 85 h shows, on Mössbauer spectra, the disappearance of the paramagnetic contribution and the formation of a magnetic contribution characteristic of the iron, indicating an apparent de-mixing of the disordered phase.

The DSC curve of the milled FeCr powder mixtures at 190 h no longer exhibits the crystallization peak at 580 °C (figure 12). It seems therefore that a crystallization of the paramagnetic contribution has occurred during the milling. However crystallization is not



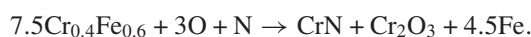
**Figure 12.** DSC curve ( $10 \text{ K min}^{-1}$ ) of the milled  $\text{Fe}_{60}\text{Cr}_{40}$  powder mixture.

evidenced by the XRD pattern, probably because the precipitates have a very small size. Amorphous alloy crystallization by mechanical sollicitation has already been observed, notably during the milling of an amorphous ribbon [30, 31].

Furthermore, a very broad exothermic peak is obtained at  $700^\circ\text{C}$ . To characterize this peak, the milled powder was annealed for 5 h at  $700^\circ\text{C}$ . After this annealing, the Mössbauer spectra was constituted of only a sextuplet corresponding to pure iron (figure 13). In addition, the XRD pattern confirms that the whole sample is crystallized in the form of pure iron and CrN nitrides (figure 14). Some peaks are not well characterized, but could relate to poorly crystallized FeCr oxides.

The observed exothermic peak at  $700^\circ\text{C}$  is therefore probably due to the precipitation of the chromium nitrides and oxides. This seems to be in agreement with results of neutron diffraction on an amorphous-type structure obtained by MA of  $(\text{Cr}_{0.7}\text{Fe}_{0.3})$  [22], which show that nitrogen preferentially surrounds the chromium.

Finally, the observed de-mixing could be the result of a preferential nitrogenation and oxidation reaction of the type

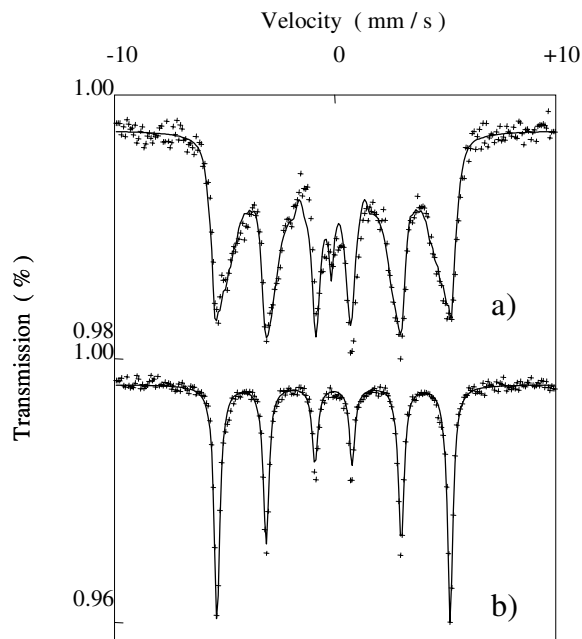


The presence of precipitates, connected with small grain size, increases the hardness and the brittleness of the material. The size of powder particles therefore decreases from  $15 \mu\text{m}$  at 85 h to  $<1 \mu\text{m}$  at 190 h.

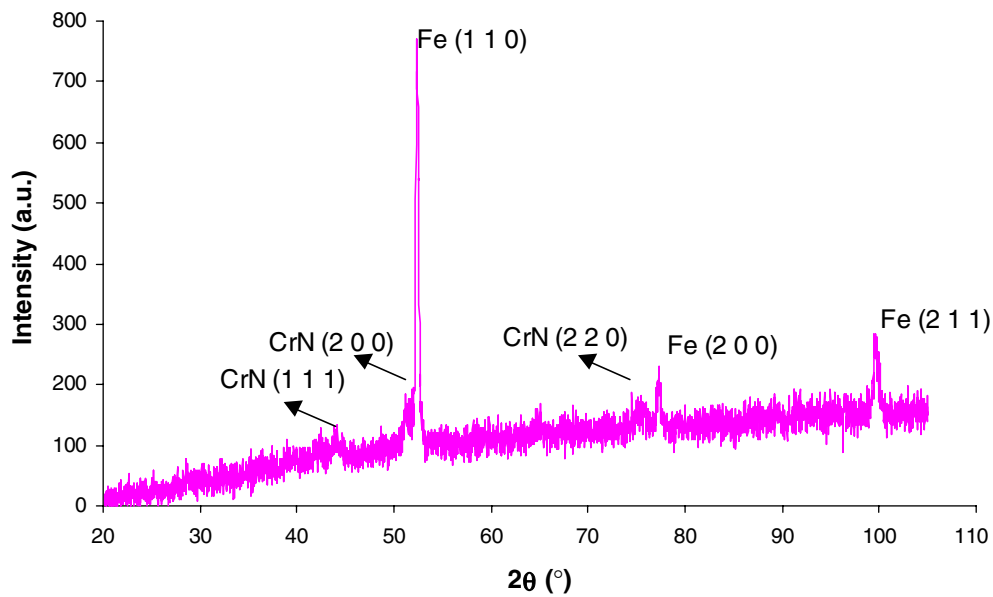
This precipitation occurs when the incorporated quantity of oxygen and nitrogen is enough to order the whole material. In this case, the energy provided to the system no longer contributes to create the chemical or topological disorder, but to crystallize the amorphous structure.

## 6. Conclusion

The paramagnetic contribution obtained during MA of an Fe and Cr mixture has a very disordered structure attributed to the presence of nitrogen and oxygen. We interpreted this contribution as an atomic mixture of amorphous  $\text{FeCr} + \text{O} + \text{N}$ . Oxygen and nitrogen incorporated during the milling would play the role of amorphizing elements. This very disordered zone crystallizes at  $580^\circ\text{C}$  with the precipitation of nitrides or phases very rich in chromium being able to contain oxygen.



**Figure 13.** Mössbauer spectra before (a) and after (b) annealing for 5 h at 700 °C of Fe<sub>60</sub>Cr<sub>40</sub> powder mixture at 190 h milling time.



**Figure 14.** XRD patterns after 190 h of milling time and after annealing for 5 h to 700 °C.

Moreover, after very long milling times, we have evidenced a de-mixing reaction, which would result in preferential oxidation and nitrogeation within the very disordered structure.

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