



Magnetic structures developed under milling in $\text{Al}_{0.4}\text{Fe}_{0.6}$

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The intermetallic compound $\text{Al}_{0.4}\text{Fe}_{0.6}$ in its ordered B2 phase has been ground under Ar in a ball-milling device up to the completion of the solid state reaction when a steady state was reached. The system transformation has been examined by X-ray diffraction and transmission Mössbauer spectroscopy, which show the development of two magnetic subspectra as milling progresses. The evolution of these magnetic components under annealing treatments at moderate temperatures was followed by Mössbauer spectroscopy and differential scanning calorimetry. The associated magnetic structures are interpreted in terms of creation and recovery of antiphase boundaries and antisite defects.

1. Introduction

Disordering of *bcc* intermetallics with B2 (cP2-CsCl) structure by mechanical work is a well-known phenomenon and the stability of these compounds under mechanical milling has been extensively examined in the last decade [1–7]. It has been established that B2 compounds like AlFe, AlRu, and AlNi do not amorphize under milling but undergo a transition to a metastable partially disordered state accompanied by grain and domain size reduction and microstrain accumulation. In the case of AlFe, a pioneer work from Huffman et al. [8] reported the modifications induced by severe cold work (crushing) in a series of $\text{Al}_{1-x}\text{Fe}_x$ ($0.5 \leq x \leq 0.7$) compounds. Their results indicated that crushing creates, through plastic deformation, a large number of antiphase boundaries (APBs) leading to antiphase domains with average linear dimensions of about six atomic distances. As is well known, plastic deformation takes place in this system mainly by the slip of {110} planes in the $\langle 111 \rangle$ direction [9].

After prolonged milling, $\text{Al}_{1-x}\text{Fe}_x$ compounds reach a steady state which is characterized by a small value of the long range order parameter S , that depends on temperature, composition and milling intensity [1,5,6,10]. As has been pointed out [11], this S value, normally obtained from diffraction techniques, should not be interpreted as necessarily implying an homogeneous disorder. Some authors have interpreted [1,12] the observed transformation as an out-of-equilibrium order–disorder transition: B2 \Rightarrow A2 (cI2-W) induced by the external mechanical forcing which repeatedly creates APBs. Other authors [4,7,13] have simply invoked the creation during the mechanical milling of excess antisite defects (AS), vacancies (V) or triple defects (T) to explain the observed changes.

The local order is also altered and this has direct consequences on the magnetic properties of the system. The magnetic moment of a given Fe atom is determined primarily by its nearest neighbour (nn) configuration: it remains essentially constant for up to 3 nonmagnetic (Al) neighbours and falls rapidly to zero between 4 and 5 Al nn's [8]. In the fully ordered B2 phase ($S = 1$) only a small fraction of Fe atoms, $(x - 1/2)/x$, bears a magnetic moment and their mutual separation is large enough to avoid magnetic coupling between them. Disordering not only affects the coordination of Fe atoms, which may thus develop a magnetic moment, but also modify their relative distances allowing their magnetic coupling. The associated magnetic properties are apparent for Al_{1-x}Fe_x compounds with $x > 0.5$ and have been studied in milled [5,14–16] and plastically deformed [8,17] samples.

Mössbauer effect (ME) spectroscopy on ⁵⁷Fe, may prove useful in the study of these mechanically induced transformations due to its ability of sensing the surroundings of Fe atoms. From the ME spectra, information about the magnetic hyperfine field B , electric quadrupole splitting (Δ) or shift (ε) and the isomer shift (δ) at a given Fe site, can be obtained. The observed hyperfine field in metallic systems is usually attributed to two effects: core polarisation (CP), i.e., induction of a net spin density in the inner s-shells by unpaired outer (3d) electrons and conduction electron polarisation (CEP) due to the 4s electron polarisation by exchange interactions with the 3d electrons and mixing with the 3d band [18]. In spite of the complex nature of this hyperfine field, a correlation between its value and the number of nonmagnetic neighbours of the central Fe atom has been established based on experimental as well as theoretical grounds. The isomer shift value also depends strongly on the number and nature of neighbours while quadrupole effects depend besides on the spatial distribution of these neighbours.

The combination of this local information with that coming from X-ray diffraction (XRD) should help to understand the modifications induced by milling on these compounds. On the other hand, differential scanning calorimetry (DSC) studies allow to follow the evolution of the system in the way back towards the equilibrium state giving indirect information about the amount and nature of the induced disorder during milling.

We present here results on the mechanical milling of the intermetallic compound B2-Al_{0.4}Fe_{0.6} and on its further thermal annealing at moderate temperatures, obtained with ME spectroscopy, XRD and DSC, with the aim of contribute to the understanding of the mechanically induced transformation to a metastable disordered state in B2 intermetallics.

2. Experimental

The starting intermetallic compound Al_{0.4}Fe_{0.6} was prepared by heating at 1000°C a mixture of adequate quantities of pure Al (Johnson–Matthey 0.995) and Fe (Fluka 0.995) powders, in evacuated ($p \leq 3 \cdot 10^{-6}$ mbar) quartz ampoules. The resulting ingot was ground and annealed in vacuum for 72 hours at 550°C in order to remove the remaining stress and to improve the degree of order.

Powder batches of 250 mg each, together with one chrome steel ball ($\varnothing = 9$ mm), were sealed into chrome steel cylindrical vials (5 cm^3) under Ar atmosphere, after several Ar purge. They were then mechanically ground in a Retsch MM2 horizontal vibratory mill operating at 25 Hz during time intervals from 1 minute to 1 hour. Under these conditions, a milling intensity $I = \nu Mv/m$ [19] of 380 m/s^2 may be estimated, with ν the impact frequency, M the ball mass, v the maximum ball velocity and m the powder mass. A batch of 1 g of powder was milled with a larger ball ($\varnothing = 12$ mm), within a 10 cm^3 cylindrical vial, at 29 Hz ($I = 300 \text{ m/s}^2$) under the same ambient conditions during 12 hours. This sample was repeatedly annealed at fixed temperatures ranging from 90 to 250°C , in dynamic vacuum ($p < 3 \cdot 10^{-6}$ mbar) during 1 hour each time.

After each milling run, XRD patterns were obtained using a Philips PW1710 diffractometer with Cu $K\alpha$ radiation in reflection geometry. All the obtained samples, milled and/or annealed, were characterized by ME spectroscopy under transmission geometry with a conventional apparatus employing a $^{57}\text{CoRh}$ radioactive source. Some milled samples were thermally analysed with a Shimadzu DSC, under dried N_2 flux (20 ml/min) in capped Pt pans, at different heating rates: 10, 20, 40 and 80 K/min.

3. Results

All the reflections expected for a *bcc* structure with B2 ordering are clearly seen in the XRD pattern of the starting material. As milling proceeds, the intensity of the superstructure reflections, those with odd $h + k + l$, decreases as a consequence of disorder. Additionally, all the peaks broaden, reflecting the grain and domain size reduction and the increase in stored microstrain. The diffractograms were fitted refining simultaneously the lattice constant a and two parameters, U and Y , related to the peak breadth and used to estimate respectively the *rms* strain $\varepsilon = 0.5\sqrt{U}$ and the average size of coherent regions for diffraction $L = 0.9\lambda/Y$ [6]. Furthermore, if the lattice is described as two interpenetrated simple cubic superlattices with different abundance of Fe and Al atoms and homogeneous disorder is assumed, the occupancy probabilities P_{Fe}^1 and P_{Fe}^2 may also be fitted. Then, an average value of the long range order parameter S can be evaluated using [20]:

$$P_{\text{Fe}}^1 = x + (1 - x)S = 1 - P_{\text{Al}}^1 = 2x - P_{\text{Fe}}^2.$$

Figure 1 displays the evolution of the fitted lattice constant and long range order parameter with milling time t_m , both showing a smooth variation towards their steady state values. In turn, the *rms* strain increases rapidly in the first 3 minutes of milling and remains practically constant around 1.6% afterwards and the mean grain size reduces from 500 to a minimum of 50 nm.

ME spectra after different t_m are displayed in figure 2. Initially, a broad absorption peak at low velocities, characteristic of paramagnetic Al-Fe phases, may be observed

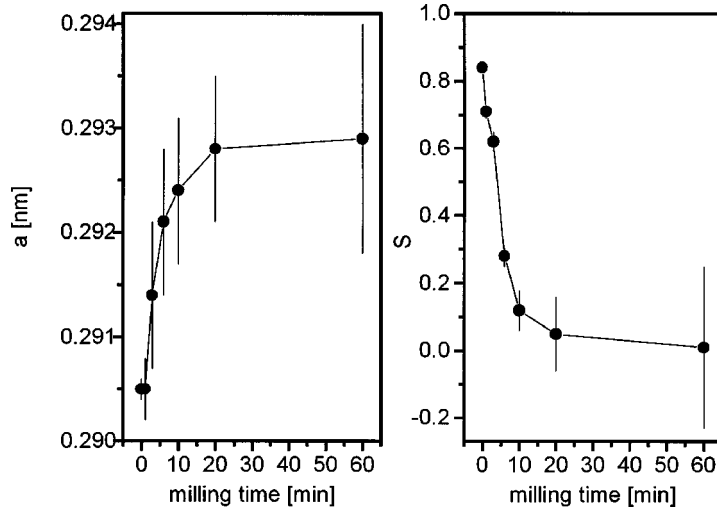


Figure 1. Evolution of lattice constant and long range order parameter with milling time, t_m .

without any trace of ferromagnetic components. As milling progresses a complex magnetic spectrum develops. Also shown in this figure are the spectra obtained after annealing a milled sample at increasing temperatures showing the reverse effect, a gradual disappearance of the magnetic spectral components.

To analyse these spectra several kind of fits were attempted using standard least-squares routines and including either broadened Lorentzians, Voigt profile lines [10,22] or model-independent hyperfine field distributions (histograms) [21]. The best agreement with the experimental data was obtained when fitting with three components corresponding to two magnetic and one quadrupole interactions, described by Gaussian distributions of Lorentzian sextets or doublets (Voigt profiles). Each magnetic interaction was then characterized by mean values of the hyperfine field B_i , its quadratic deviation σ_i , the isomer shift δ_i and the quadrupole shift ε_i . In turn, the quadrupole interaction was defined by mean values of the quadrupole splitting Δ , its quadratic deviation σ and the isomer shift δ and a linear correlation coefficient α , relating δ and Δ . The relative fractions of each interaction (f_1 , f_2 and $f_Q = 1 - f_1 - f_2$) were also fitted together with the above mentioned parameters.

The evolution of some of these parameters with milling time and annealing temperature is shown in figures 3–5. For instance, the fraction of the magnetic components increases as milling proceeds, in detriment of the quadrupole one, reaching in total more than 80% of the sample. The reverse behaviour is seen as a function of annealing temperature, the magnetic subspectra having almost disappeared after a heat treatment at 250°C. It is worth noticing that in spite of the complicated shape of the spectra the two magnetic components may be clearly distinguished in them. Indeed, when fits were attempted using a model-independent hyperfine field distribution [21], the resulting histogram $P(B)$ showed a bimodular shape.

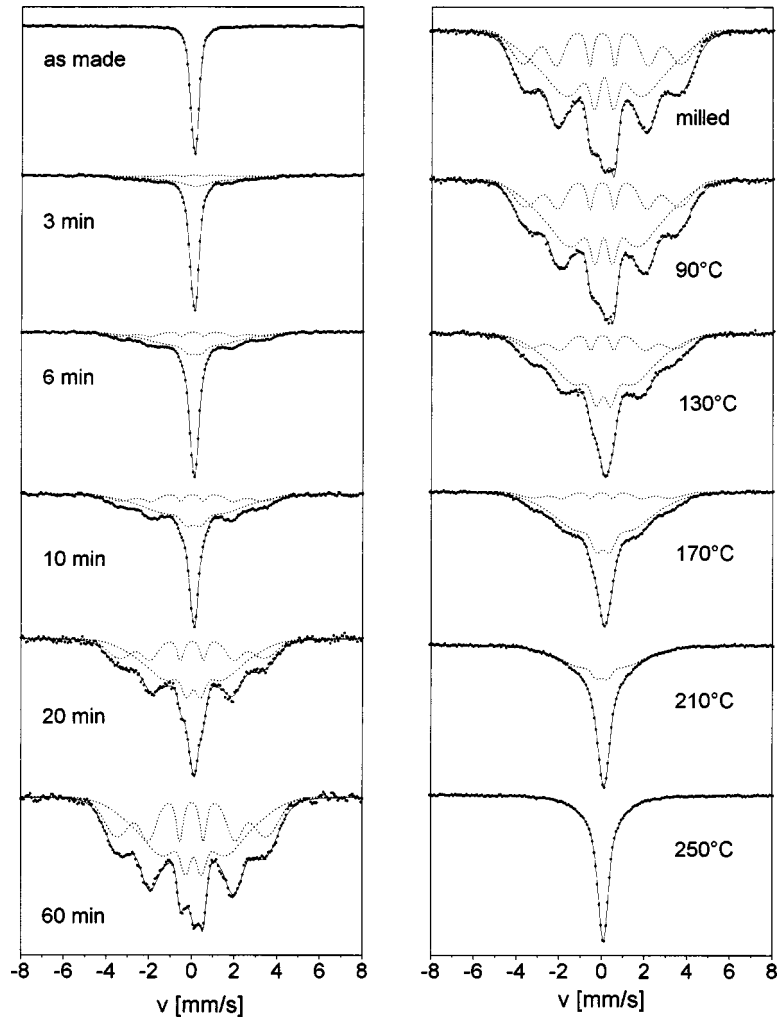


Figure 2. ME spectra after milling during various periods and after annealing at increasing temperatures. The fitted magnetic components are also shown.

The calorimetric signal measured at a heating rate of 20 K/min on a sample milled during 12 hours is shown in figure 6. Several overlapping thermal effects may be identified. The heat release starts at about 100°C showing a baseline shift and an exothermic peak around 200°C or less. The enthalpy associated with this transformation is about 11 J/g. A second overlapping effect peaks at 305°C and a third, well defined, peak is seen at 447°C. This is consistent with previous observations in this system [10] where three stages have been recognized and associated respectively with reordering, vacancy migration recovery and dislocation cross slip and climb recovery. The same DSC profile was observed at different heating rates 10, 40 and 80 K/min, all the characteristic temperatures shifting to higher values on increasing the heating rate.

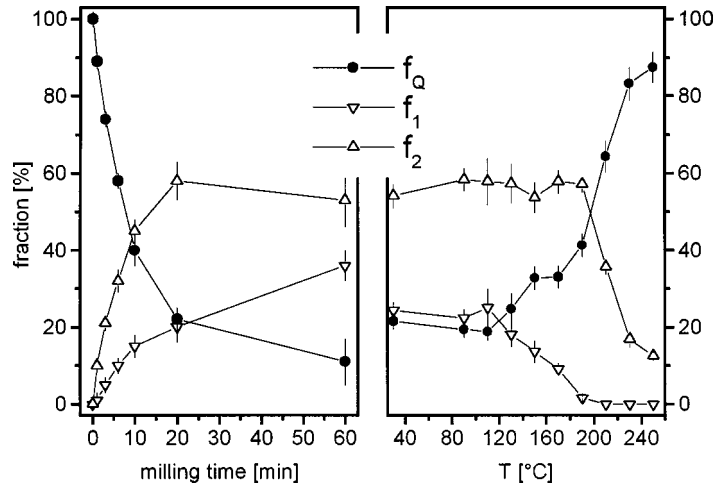


Figure 3. Evolution of the fitted fractions of the various components in the ME spectra.

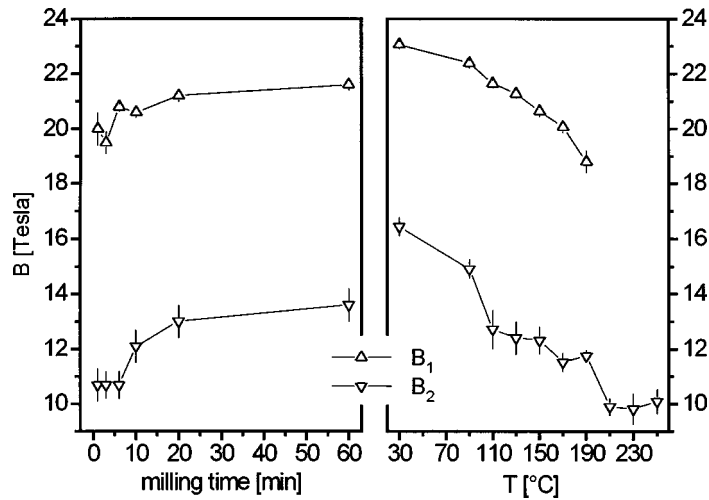


Figure 4. Evolution of the fitted mean hyperfine magnetic field with milling time and annealing temperature.

4. Discussion

From the ME results it is evident that milling causes the instant development of magnetism. Two broadly distributed magnetic components are necessary in order to get satisfactory fits both during milling and annealing sequences (see figure 2). Once established, these spectral components change very little, the main effect being the variation of their relative populations that increase monotonically with milling time and decrease by steps with annealing temperature (see figure 3). Among these components, the less abundant is characterized by a mean field B_1 around 20–21 T and an average isomer shift around 0.11 mm/s. It may be associated with Fe atoms having Fe-rich environ-

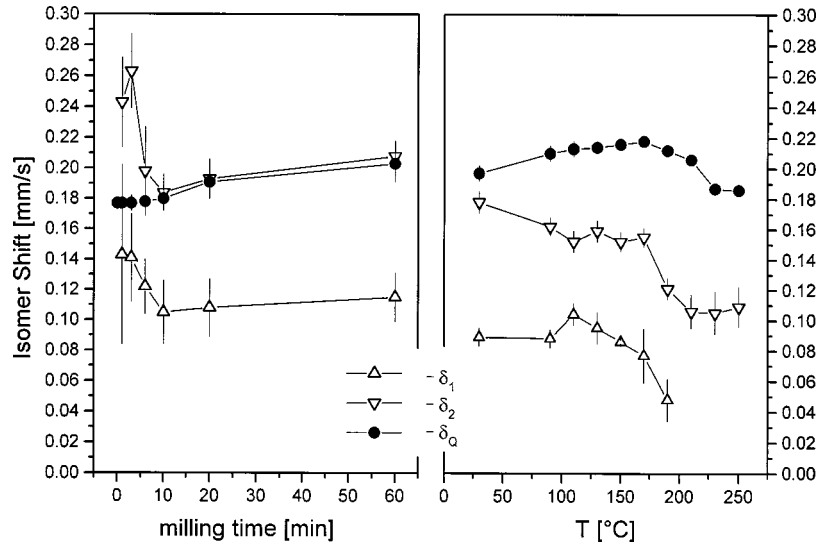


Figure 5. Evolution of the fitted mean isomer shift with milling time and annealing temperature.

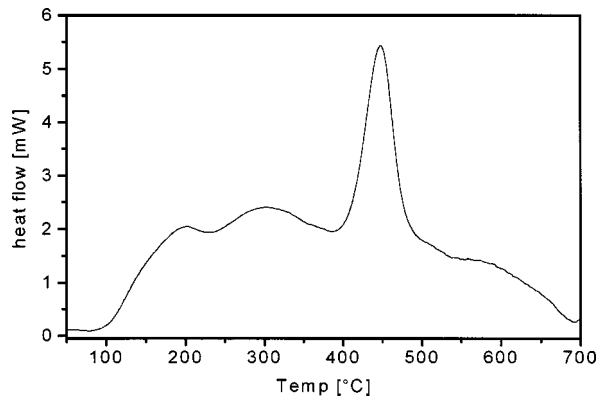


Figure 6. Calorimetric scan at a rate of 20 K/min on a sample milled during 12 hours.

ments: more than 4 Fe nn on the average [7]. In turn, the second and more distributed one, has a mean field value B_2 varying between 11 and 13 T and an average isomer shift around 0.19 mm/s and could be assigned to Fe atoms with Fe-poorer environments: having on the average around 3 Fe neighbours.

The remaining quadrupole component does not change very much with milling and could be assigned to Fe atoms not bearing a magnetic moment and to those that, in spite of having a magnetic moment, behaves paramagnetically. This would be the case for isolated atoms (unpolarized atoms) and for groups of atoms not sufficiently numerous to orient themselves (superparamagnetic clusters). A crude analysis of this situation could be made as follows. In the as milled sample, 80% of the Fe atoms contributes to the magnetically split subspectra, 48% corresponds to the low field component and 32% to

the high field one. Average magnetic moments of $1.3 \mu_B$ and $1.9 \mu_B$ per Fe atom, may be attributed to the Fe atoms experiencing such interactions [8,18]. If it is assumed that the Fe atoms contributing to the quadrupole subspectrum carry no magnetic moment, the average magnetic moment per Fe atom in the sample would be $1.22 \mu_B$. On the other hand, magnetization measurements carried out on a similar system [5] yield an average magnetic moment of $1.26 \mu_B$. We may thus conclude that a small fraction of that 20% Fe atoms might have a magnetic moment but behaves paramagnetically.

In order to interpret these results we recall some structural properties of these compounds. For $x > 0.5$, the ordered B2 Al_{1-x}Fe_x phase ($S = 1$) may be viewed as two interpenetrated simple cubic superlattices, one of them fully occupied by Fe atoms (Fe¹) and the other partially by Al and partially by the remaining Fe atoms (Fe²) which may be thought as constitutional AS. In the present case ($x = 0.6$), Fe¹ atoms will have an average coordination of 6.4 Al and 1.6 Fe while Fe² ones will be surrounded solely by 8 Fe neighbours, developing a magnetic moment. These Fe² atoms are randomly distributed and will not necessarily interact ferromagnetically with other Fe atoms, unless they form a sufficiently large cluster. Homogeneous disorder will modify both the Fe¹ and Fe² fractions ($1/2 + S/3$ and $1/2 - S/3$, respectively) and their average coordination, which will include $4.8 - 3.2S$ or $4.8 + 3.2S$ Fe neighbours. On the other hand, the slip of $\{110\}$ planes in the $\langle 111 \rangle$ direction, creating APBs, will leave the Fe atoms at both sides of the APB in optimal situation to behave ferromagnetically [8,17]. It is worth noticing that even for an otherwise ordered sample ($S = 1$): (i) in the sliding operation that creates the APB, the Fe¹ atoms change, on the average, from having 1.6 to 3.2 Fe near neighbours, just enough to develop a magnetic moment; (ii) these Fe¹ atoms are nearest neighbours of the homologous Fe¹ atoms at the other side of the APB, with which they may couple ferromagnetically, thus forming planar magnetic clusters (see [17, figure 13]).

It is rather well established that at least in the first stages of milling, these compounds absorb the induced plastic deformation through the sliding along $\{110\}$ planes in the $\langle 111 \rangle$ direction, creating planar regions of APBs between pairs of superpartial dislocations [11]. It seems then reasonable to assign the majority magnetic component B_2 to the magnetic clusters generated at the APBs. They appear immediately after milling and its fraction increases linearly for short milling periods (up to at most 20 minutes) and finally saturates due to the interference between slipped planes. In turn, the minority magnetic component B_1 may be associated to those Fe² (constitutional and induced AS) which bears a higher magnetic moment and are either polarized by the APB clusters [17] or are grouped, as a result of milling, in sufficiently large clusters.

These assignments are supported by previous results on related compounds [22]. It is worth mentioning that in Al_{0.45}Fe_{0.55} the same two magnetic subspectra appear after milling, but in different proportion (see figure 7). The ratio f_1/f_2 is always lower than in the present case and this is consistent with the lower fraction of AS in the Fe poorer system. Furthermore, in the case of Al_{0.50}Fe_{0.50} no magnetic interaction is detected, at least at room temperature, probably as a consequence of the fact that Fe¹ atoms on the APBs would have only 2 Fe neighbours on the average and hardly develop a magnetic moment.

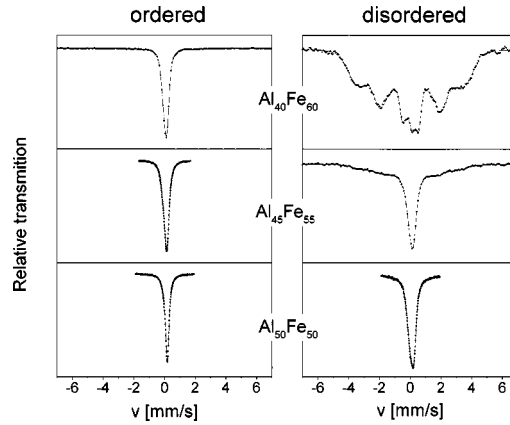


Figure 7. ME spectra of ordered and disordered $Al_{1-x}Fe_x$ compounds with $x = 0.50, 0.55$ and 0.60 .

The behaviour of these magnetic components under thermal annealing may also be interpreted under the above assignments. The first interaction (B_1) starts to disappear at about 100°C when vacancies become mobile for very short distances [11,16]. The subsequent local reordering has two immediate consequences: (i) the displaced atoms lose or diminish their magnetic moments due to the change of their coordination; (ii) some magnetic clusters dissociate and/or escape from the polarizing effect of the APB zones. At 200°C this component has completely disappeared, just remaining the almost unchanged magnetic component originated in the APBs. Somewhat higher temperatures are necessary to eliminate this component. As several authors have reported [8,11] dislocations become mobile in these systems at about 200°C , thus promoting the APBs recovering and the extinction of the associate magnetic clusters. Nevertheless, the recovery is not complete and a small magnetic fraction survives needing higher annealing temperatures to disappear. This would probably be a consequence of the presence of tangled dislocations.

5. Conclusions

Room temperature milling of $Al_{0.4}Fe_{0.6}$ at low intensity ($I \leq 400 \text{ m/s}^2$) leads to a stationary state with an apparent lack of long range order ($S = 0$). The disordering process is accompanied by the development of a complex magnetic structure. Most of the magnetic atoms are located at the mechanically induced $\{110\}$ APBs, forming almost two-dimensional magnetic zones, that surround less defected regions where, isolated as well as clustered, magnetic atoms exists. This inhomogeneous picture of the disorder distribution confirms our previous findings in related systems [6,22].

Thermal treatments at moderate temperatures produce the removal of these magnetic structures in a distinct way. In particular, the APBs magnetic zones need that dislocations become mobile to disappear. As a consequence the mobility of vacancies and dislocations may be distinguished in the early stages of the reordering process.

Further studies are in progress in order to elucidate the remaining stages in the recovery of this kind of systems and to take advantage of the peculiar magnetic metastable structures that may be obtained in them.

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