Order-disorder transformation in Fe-Al under ball milling

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(Received 10 February 1995; revised manuscript received 18 April 1995)

Ball-milling experiments of the ordered intermetallic compound $Fe_{50}Al_{50}$ are carried out in a calibrated vertical vibrating frame grinder at various temperatures T and milling intensities I, defined as the momentum transferred by the ball to the unit mass of powder per unit time. The long-range order (LRO) parameter, as quantified by x-ray diffraction, decreases as a function of milling time and reaches a steady-state value which is a function of T and I. The time evolution of the LRO parameter can be fitted to a simple model of order-disorder transition under external forcing, in which the atomic exchanges occur because of two mechanisms: the forced atomic jumps, the frequency of which is found to be proportional to I and the thermally activated jumps, the frequency of which is found to be a linear function of I. The forcing parameter, defined as the ratio of the latter two jump frequencies, is found to be the control parameter of the steady degree of LRO achieved under ball milling. Moreover, the kinetic path of the LRO parameter depends on the milling intensity and milling temperature and is in semiquantitative agreement with the model.

I. INTRODUCTION

Ball milling as well as irradiation by energetic particles are known to bring materials far from their equilibrium state. Alloys under ball milling or irradiation are sometimes named "driven alloys."¹ It is now established that the dynamical steady state achieved by such systems is a function, for a given composition, of the temperature and the intensity of the forcing. In the case of alloys under irradiation, the forcing parameter is known to be, to a first approximation, proportional to the ratio of the frequency of two types of atomic jumps: those induced by nuclear collisions and those resulting from thermally activated processes.

In the case of ball milling, the situation is far less clear: indeed the effect at the atomistic scale of the collisions of the milling balls with the powder is poorly described. However, Chen *et al.*² have established that the steadystate structure achieved in Ni_xZr_y compounds (x/y=5/1,5/2,10/7,1/1,1/2) in a vibrating frame grinder depends on the composition, the milling temperature, and a "specific milling intensity" defined as the momentum transferred by the ball to the unit mass of powder per unit time:

$$I = \frac{M_b V_{\text{max}} f}{M_p} \ (\text{m/s}^2) , \qquad (1)$$

where M_b is the mass of the ball, V_{max} the maximum velocity of the ball, f the impact frequency, and M_p the mass of powder in the vial.

The purpose of this work is to establish the way ballmilling induced transitions depend on the milling intensity and milling temperature. Since the mechanism of crystal to amorphous transition is still not well established at the atomistic level,³ we have chosen a much simpler and better understood transition: the order-disorder (A2-B2) transition in FeAl.

The stability of B2-type compounds under ball milling has been extensively studied for the past ten years. At room temperature, some B2 compounds [AlRu,⁴ SiRu, NiTi, and CuEr (Ref. 5)] undergo a decay of the longrange order parameter, as measured using x-ray diffraction (XRD), to a steady value. This value is rather high and depends on the alloy: 0.9, 0.75, and 0.65 for respectively CuEr, SiRu, and AlRu. Since the maximum milling time was 24 h only (to prevent welding), it is possible that the ultimate degree of order observed does not correspond to a steady-state value. In the same way, two other stoichiometric B2 compounds CoGa (Ref. 6) and CoAl (Ref. 7) were partially disordered in a modified vertical vibrating frame grinder. Measurements of magnetic properties have shown that mechanical attrition was generating a triple defects disorder, leading B2 compounds to a disordered state. In another way, the B2 compound, CoZr ball milled in a Invicta vibratory mill⁸ amorphizes after 24 h, but no decrease of the LRO parameter occurred prior to amorphization. The influence of the milling device and temperature were studied on TiNi (Ref. 9): no long-range order (LRO) data were reported, but amorphization was studied. The time required for amorphization was found to depend on the milling temperature and a "milling energy": for the less energetic milling device, amorphization did not occur.

As a summary, B2 intermetallic compounds under ball milling can undergo two types of disordering: chemical disordering (characterized by the decrease of the LRO parameter) and topological disordering, leading to amorphization. One of the two steps is observed depending on the compound and the milling device. In the present work, we focus on the first step, chemical disordering, since it is simple enough to be modeled theoretically.¹ For a given milling device, it is known that the steady value of the LRO parameter (S_{steady}) depends on the compound.^{4-7,10,11} However, the influence of the milling intensity and temperature on S_{steady} and the kinetic path towards S_{steady} are still poorly described.

The paper is organized as follows: In Sec. II we describe the experimental procedure used in the present study, our results are presented in Sec. III, and Sec. IV reports the theorical analysis of our results.

II. EXPERIMENTAL PROCEDURE

FeAl was chosen as a model compound because it is known not to amorphize in a large range of composition¹² and the order-disorder (A2-B2) transition under classical thermal conditions is well described and understood.¹³ Moreover, the B2 structure exists in a large range of composition. The Fe₅₀Al₅₀ composition was chosen for a practical reason: for higher Fe content, the powder once disordered becomes ferromagnetic at room temperature and sticks to the vial; the efficiency of the milling decreases in an uncontrolled manner.¹⁴ This is not the case for Fe₅₀Al₅₀.

Ball-milling treatments were performed in the instrumented vibrating frame grinder (Pulverisette 0, FRITSCH) which Chen et $al.^2$ have set up recently to identify and define the milling intensity (Fig. 1). The device consists of a tungsten carbide vial vibrating at 50 Hz and containing the ball (1 kg Tungsten Carbide or 500 g hardened steel) and the powder. The amplitude of vibration (either 0,5 or 1 or 1,5 mm) induces an up and down movement of the ball. We have checked that when at least 2 g of powder are introduced in the vial, the collision between the ball and the powder is purely plastic and the movement almost periodic.¹⁵ The milling device has been recalibrated¹⁵ in order to confirm the values of the milling intensity, I [given by Eq. (1)] as a function of milling conditions: milling intensities, in our device, range from 650 to 4500 m/s². The milling temperature can be controlled in the range 293-523 K by means of heating tapes fixed around the bowl; the heating is regu-



lated by a thermocouple inserted into the bottom of the vial. For preventing oxidation or nitruration of the powder, the vial is outgassed (10^{-5} mbar) prior to milling and then hermetically sealed up (a vitton seal prevents leakage from the atmosphere during the whole milling treatment). At the end of the milling treatment, the microstructure of the as-milled powder can be quenched by circulating liquid nitrogen in a jacket located in the bottom of the vial: cooling from 373 to 150 K requires typically less than one minute.

The as-milled powder is characterized by x-ray diffraction using Cu K α radiation (and a back monochromator). From XRD patterns, the degree of LRO is calculated by comparing the intensities of the fundamental (h+k+l=2n) and of the supperlattice (h+k+l)=2n+1) peaks; (200) and (100) reflections have been chosen to prevent any texture effect. To improve the precision on LRO parameter, the counting time was increased in the vicinity of the (100) and (200) peaks $(\theta_{step} = 0.005^\circ; t = 10 s)$. However, for LRO parameter values lower than 0.3-0.4, the detection of the (100) peak becomes very difficult and the LRO values are not reliable. The crystallite size (d) is calculated from the FWHM (full width at half maximum) measurements, using Scherrer's formula for the fundamental peaks (110) or (200); the ordered domain size (ϕ) is estimated in the same manner from the supperlattice peak (100). Whenever domain size is compared to crystallite size, the latter is estimated from the (200) peak in order to eliminate texture effects.

The thermal stability of ball-milled powders has been examined by differential thermal analysis (DTA): a SETARAM (TAG 24) equipment was used with a heating rate of 5 °C/min, under a flow of pure argon (3 l/h) using platinum crucibles. The reordering temperature of the as-milled powder could be estimated in this way.

The evolution of the microstructure and of the crystallite size in the course of milling is followed by transmission electron microscopy (TEM) observations in a Philips CM20. The as-milled powder, dispersed in ethanol, is spread onto a carbon-coated grid. After drying, the thinnest particles can be observed. Most of the TEM work is still underway.

The parent compound $Fe_{50}Al_{50}$ is prepared by levitation melting 20 g of high purity Fe and Al (99.995%) under helium atmosphere. The homogeneity of the intermetallic compound is optimized by remelting the ingot at least three times and then annealing for 12 h at 973 K under good vacuum (2. 10^{-6} mbar). The annealed ingots are crushed into powders in a hardened steel mortar using a uniaxial press, and sieved to 400 μ m. Prior to milling, powders are annealed 3 h at 773 K under good vacuum (2. 10^{-6} mbar) in order to standardize the long-range order parameter and to relax internal stresses.

III. EXPERIMENTAL RESULTS

FIG. 1. Instrumented vertical vibrating frame grinder (see text) (Ref. 2).

All experiments performed in this study are listed in Table I.

| | Milling conditions | | | | Long-range order | | Fit to Eq. (2) | | | | |
|-------|--------------------|--------------|------------------|-------------|------------------|------------------|----------------------------|----------------------------|---------------------|---------|------------------|
| Label | Ι | Т | t _{max} | Number of | S_0 | $S_{\rm steady}$ | Γ_t | Γ_b | Γ_b/Γ_t | T/T_c | Type of kinetics |
| | $(m s^{-2})$ | (K) | (h) | experiments | | - | (10^{-5} s^{-1}) | (10^{-5} s^{-1}) | γ | au | (see Sec. IV C) |
| 1 | 1000 | 308 | 80 | 7 | 1 | 0 | 0.47 | 0.94 | 2 | 0.34 | (b) |
| 2 | 2000 | 308 | 80 | 7 | 1 | 0 | 0.72 | 0.12 | 2.25 | 0.34 | (b) |
| 3 | 2800 | 308 | 60 | 5 | 1 | 0 | 0.97 | 0.23 | 2.35 | 0.34 | (c) |
| 4 | 4100 | 308 | 20 | 7 | 1 | 0 | 1.2 | 0.32 | 2.6 | 0.34 | (d) |
| 5 | 2000 | 348 | 80 | 7 | 1 | 0.50 | 1.4 | 1.9 | 1.45 | 0.39 | (a) |
| 6 | 2000 | 373 | 80 | 6 | 1 | 0.78 | 2.2 | 1.4 | 0.65 | 0.41 | (a) |
| 7 | 4100 | 348 | 80 | 5 | 1 | 0.37 | 1.9 | 3.1 | 1.62 | 0.39 | (a) |
| 8 | 4100 | 373 | 80 | 6 | 1 | 0.62 | 2.5 | 2.6 | 1.05 | 0.41 | (a) |
| 9 | 4100 | 348 | 40 | 1 | 0 | 0.35 | | | | 0.39 | |
| 10 | 4100 | 358 | 40 | 1 | 0 | 0.48 | | | | 0.40 | |
| 11 | 4100 | 373 | 40 | 1 | 0 | 0.54 | | | | 0.41 | |
| 12 | 4100 | 423 | 40 | 1 | 0 | 0.85 | | | | 0.47 | |
| 13 | 4100 | 473 | 40 | 1 | 0 | 0.90 | | | | 0.53 | |
| 14 | 2000 | 333 | 40 | 1 | 0 | 0.1 | | | | 0.37 | |
| 15 | 2000 | 338 | 40 | 1 | 0 | 0.38 | | | | 0.37 | |
| 16 | 2000 | 343 | 40 | 1 | 0 | 0.48 | | | | 0.38 | |
| 17 | 2000 | 348 | 80 | 4 | 0 | 0.47 | | | | 0.39 | (a) |
| 18 | 2000 | 373 | 80 | 4 | 0 | 0.76 | | | | 0.41 | (a) |
| 19 | 2000 | 398 | 40 | 1 | 0 | 0.82 | | | | 0.44 | |
| 20 | 2000 | 423 | 40 | 1 | 0 | 0.87 | | | | 0.47 | |
| 21 | 2000 | 473 | 40 | 1 | 0 | 0.94 | | | | 0.53 | |
| 22 | 2000 | 523 | 40 | 1 | 0 | 1 | | | | 0.58 | |
| 23 | 2000 | 323 | 40 | 1 | 0 | 0 | | | | 0.36 | |
| 24 | 4100 | 333 | 40 | 1 | 0 | 0 | | | | 0.37 | |

TABLE I. Parameters values for all the milling experiments performed on FeAl, in the present study.



FIG. 2. Typical x-ray-diffraction patterns for increasing milling time, with a milling intensity $I = 2000 \text{ m/s}^2$ at 298 K.

A. Evolution of the microstructure

As shown by scanning electron microscopy (SEM) and TEM studies,³ after several hours of milling the material consists of particles of powder. Each particle is made of sticked grains which themselves consist of several crystal-lites.

Figure 2 shows a typical sequence of XRD patterns of as-milled FeAl powder for increasing milling time at room temperature with a milling intensity of 2000 m/s^2 . Each peak can be indexed according to the ASTM (American Society for Testing and Materials) FeAl file but the intensities of the peaks are not in the proper ratio, because of a marked texture of the crystallites. With increasing milling time, superlattice peaks are broadening and their intensities decrease very quickly, whereas fundamental peaks are only broadened. The broadening of the peaks is the result of crystallite refinement and internal strain. We have neglected the latter for crystallite size calculation.

In Fig. 3, the ultimate antiphase domain size (ϕ) and crystallite size (d) are plotted as a function of milling temperature. The underlying microstructure is as follows: after some 10 to 20 h, the microstructure reaches a steady state which depends on the milling temperature, but not on the milling intensity. At lower temperatures (T < 373 K) the crystallite size remains constant $(d \approx 7)$



FIG. 3. Steady-state size of crystallites (d) and domains (ϕ) at 2000 and 4100 m/s² as a function of the milling temperature. The sizes are deduced respectively from (200) and (100) lattice spacings, using Scherer's formula.

nm) and the crystallites contain several (≈ 3) ordered domains. At higher temperatures, the crystallite and domain sizes increase with increasing temperature and become both equal at about 523 K.

Figure 4 reports the evolution of the size of the crystallites [calculated from the broadening of the (110) fundamental peak] for various milling intensities at room temperature as a function of the milling time. During the first 10 h, the crystallite size decreases abruptly and reaches a steady value, of about 12-13 nm. The steady size is not sensitive to the milling intensity. The crystallite sizes calculated from the XRD pattern are consistent with TEM observations: the contribution of the strain to the broadening of the XRD peak can therefore be safely neglected. The same behavior is observed with respect to the milling temperature in the range 308-373 K (experiments 2, 5, and 6 in Table I). Whatever the temperature, the crystallite size decreases abruptly in the first 10-20 h and reaches a steady crystallite size in the range 12-14 nm.

B. Evolution of the long-range order parameter

The most detailed studies have been performed at two milling intensities (2000 and 4100 m/s^2) at various tem-



FIG. 4. Steady-state crystallite size at 308 K as a function of the milling intensity [as deduced from (110) lattice spacing].

peratures (Table I). These results show the existence of steady values of the LRO parameter (S_{steady}) depending on the milling intensity and temperature. Further experiments carried out at various temperatures and milling intensities (Table I) allowed to follow the kinetic path towards S_{steady} .

1. Steady-state long-range order

Figure 5 shows the time evolution of the LRO parameter at a milling intensity of 2000 m/s^2 , at three distinct milling temperatures in the range 308-373 K. Below 348 K, the LRO parameter decreases first continuously to a transient value and then abruptly to zero. At 348 K and above, the LRO parameter decreases rapidly to a steady value. The higher the temperature, the larger the steady value of the LRO parameter.

At a given temperature, the time evolution of the LRO depends on the milling intensity [Fig. 6(a)]: at 373 K, the LRO reaches a steady value which is lower the higher the intensity. In order to ensure that those steady states are not transient, we have performed a reordering milling treatment starting from a disordered powder obtained by first ball milling for 24 h at room temperature and at an intensity of 2000 m/s². This powder has been then milled for various milling times at 373 K at the same intensity. The LRO parameter increases up to a steady value, equal to that reached by disordering an initially ordered compound with the same milling conditions [Fig. 6(a)]. The reversibility of the order-disorder transition induced by ball milling has been also checked at 348 K [Fig. 6(b)].

As a summary, the LRO parameter reaches a steady value depending on the milling intensity and temperature. This value is unique and can be reached either starting from fully ordered or fully disordered compounds. In Fig. 7, the steady-state value of the LRO parameter (S_{steady}) is plotted versus the temperature, for two milling intensities: the steady value of the LRO parameter increases continuously with increasing temperature (for $T > T^*$). The threshold temperature T^* increases slightly with the milling intensity. Unfortunately, our device does not allow to explore a broad range of milling intensities.



FIG. 5. Time evolution of the long-range order parameter for various temperatures at a milling intensity of 2000 m/s^2 . The initial state is fully ordered (experiments 2, 5, and 6 in Table I).



FIG. 6. Time evolution of the long-range order parameter for various milling intensities. The same steady state is reached independently of the initial state, fully ordered or fully disordered; (a) at 373 K (experiments 6, 8, and 18 in Table I); (b) at 348 K (experiments 5, 7, and 17 in Table I).



FIG. 7. Dynamical steady values of the long-range order parameter at two milling intensities as a function of the temperature (experiments 9-24 in Table I).

2. Kinetic path for the long-range order

As milling proceeds, the LRO parameter decreases in a nonsteady manner (experiments 1-4 in Table I). Figure 8 represents the long-range order parameter as a function of the milling time for various milling intensities at room temperature. Two stages can be identified.

(i) For short times, the LRO parameter decreases exponentially and reaches a transient stationary state value $S^*(S^*\neq 0)$. The transient stationary state level and its duration seem both to decrease as the milling intensity increases. Moreover, when the milling intensity is larger than a threshold value, the transient stationary state disappears: the LRO parameter decreases smoothly to zero.

(ii) For longer duration, the LRO parameter decreases abruptly to zero.

As a summary, it seems that at the lowest intensities, the alloy goes through some metastable dynamical state with an intermediate degree of LRO parameter before reaching the final fully disordered steady state $(S_{\text{steady}}=0)$.

IV. DISCUSSION

A. Microstructure and long-range order

The well-known saturation of the crystallite size during ball milling is observed.¹⁶ According to the literature, the ultimate crystallite size is known to depend on the milling device¹¹ and the alloy composition.¹⁷ We have found that the ultimate crystallite size achieved by ball milling does not depend on the milling intensity in the small range of milling intensities available on our device.

The ultimate crystallite size is independent of the milling temperature in the range 298-398 K, but increases continuously at higher temperature (> 423 K). The same behavior is observed for the ultimate ordered domain size: in the range T^*-373 K (where T^* is the orderdisorder temperature at the milling intensity under study), the domain size is almost constant and it increases with temperature for T > 398 K.



FIG. 8. Time evolution of the long-range order parameter for various milling intensities, at 308 K, starting from the ordered state (experiments 1–4 in Table I).

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FIG. 9. Heat release by an as-milled powder as revealed by DTA: the broadened peak is analyzed into two peaks.

On the contrary, the evolution of the LRO parameter with time depends both on milling intensity and temperature. A reason for the decoupling between LRO and crystallite size evolution is suggested by the thermal analysis of the annealing processes in the as-milled powder (Fig. 9): a broad peak of heat release is observed in the range 343-532 K, whatever the milling conditions. This peak can be analyzed into two contributions, one centered at about 403 K, the second at 468 K. XRD analysis of annealed milled powders show that the 403 K peak is to be attributed to reordering and the 468 K peak to grain growth. Since the reordering occurs at lower temperature, the steady degree of order must result from a delicate balance between shear induced disordering and thermally activated reordering in the temperature and intensity range which has been explored in the present study. On the other hand, grain growth only operates at higher temperatures; this explains the lower sensitivity of the microstructure to the milling conditions, at least, in the range we could explore.

B. Steady degree of long-range order under ball milling

We found the dynamical steady-state value of the LRO parameter to be a function of the temperature and of the milling intensity. This situation is reminiscent of what happens in intermetallic compounds under irradiation.¹⁸ To analyze our results, we use a simple model of orderdisorder transition in driven alloys developed by Bellon and Martin.¹⁹ The model was originally built for the A2-B2 transition in the stoichiometric compound under homogeneous irradiation. The basic idea is that the LRO parameter S evolves in time as a result of the competition of two atomic displacements processes: those induced by external forcing which generate disorder and those resulting from thermally activated jumps which drive the material to its thermal equilibrium state. For the sake of simplicity, the forced displacements are modeled by nearest-neighbor exchanges. Following Ref. 19, the degree S of LRO changes as

$$\frac{dS}{dt} = 4\Gamma_t \{ (1-S)^2 [\gamma + \exp(2ST_c/T)] - (1+S)^2 [\gamma + \exp(-2ST_c/T)] \}$$
(2a)

with
$$\gamma = \frac{\Gamma_b}{\Gamma_c}$$
 (2b)

In Eq. 2(a), Γ_t is the mean frequency of thermally activated atomic jumps, Γ_b the mean jump frequency of atomic exchange imposed by the external forcing (Γ_b is called the ballistic jump frequency), and T_c the critical temperature for the order-disorder transition in the absence of external forcing; γ is called the forcing parameter.

The rate of change of S(dS/dt) as a function of S, as measured in experiments 1-8 (Table I) has been analyzed with Eq. (2). For experiments exhibiting a transient stationary state before reaching the fully disordered state (experiments 1-4 in Table I), Eq. (2) was used for the decay of S down to the transient stationary state, i.e., the part of the curve where we have most data.

In view of the crudeness of the model, we left the three parameters free for the fitting procedure: T_c (common to all experiments), Γ_b , and Γ_t . The best parameter values are given in Table I and can be summarized as follows (see Figs. 10 and 11): $T_c = 900$ K, $\Gamma_b = A_b I$, $\Gamma_t = A_t I + B_t(T)$, where A_b and A_t are constants and B_t is a function of the milling temperature; I is the milling intensity.

The above features can be understood at least qualitatively. In a first fitting procedure, T_c was left as an ajustable parameter for each experiment: T_c was found to be independent of the milling conditions, within ≈ 30 K. T_c is therefore a materials constant as it should be. We fixed it to 900 K for all experiments. The critical temperature T_c thus found is lower than that expected from the FeAl phase diagram. Despite the fact Fe₅₀Al₅₀ melts prior disordering at 1540 K, the critical temperature for the order-disorder transition can be estimated by extrapolation: it is about 1620 K.²⁰ That the "critical temperature" which enters Eq. (2) is lower than the true one implies that the driving force for reordering the disordered state is lower in the ball-milled sample than at equilibrium. This might be linked to the very small crystallite size in the milled material or to the vacancy supersaturation expected during milling: the details of such effects



FIG. 10. Ballistic jump frequency Γ_b [from Eq. (2)] for various temperatures as a function of the milling intensity.



FIG. 11. Thermally activated jump frequency Γ_t [from Eq. (2)] for various temperatures as a function of the milling intensity.

remain however to be clarified.

The ballistic jump frequency Γ_b is proportional to the milling intensity I (Fig. 10) with a proportionality constant, the "ballistic yield" $A_b = \Gamma_b / I$, independent of the temperature. This is quite in agreement with the simple idea that the disorder induced by one stroke of ball occurs in shear bands, the extension (and/or number) of which increases with the momentum transferred to the material. Indeed, the momentum transferred goes as the applied force times the duration of contact. With the units used up to now, $[\Gamma_b] s^{-1}$ and $[I] m s^{-2}$, the ballistic yield A_b is about $7.5 \times 10^{-9} s m^{-1}$. Giving a physical interpretation of this value requires a detailed description of the disordering process during the impact of the ball, which is still lacking.

The mean thermal jump frequency of atoms Γ_t depends both on the milling intensity and milling temperature as $\Gamma_t = A_t I + B_t(T)$. To a first approximation, A_t is independent of the temperature and B_t independent of the milling intensity. The thermal jump frequency of atoms is the product of the thermal jump frequency of vacancies Γ_v times the vacancy concentration $\overline{C_v}$,

$$\Gamma_t = \Gamma_v \overline{C_v} \ . \tag{3}$$

The latter can be estimated assuming the vacancies are generated at a rate proportional to the milling intensity, $G_v I$ (for the same reason as the disordering rate) and eliminated by diffusion to the crystalline boundaries. The following balance equation results:

$$\frac{dC_v}{dt} = G_v I - k_v^2 \Gamma_v (C_v - C_v^0) , \qquad (4)$$

where C_v^0 is the vacancy concentration at thermal equilibrium and k_v^2 the sink strength of grain boundaries $[k_v^2 \approx 10(a/d)^2$ with *a* the lattice constant and *d* the crystallite diameter²¹]. From Eqs. (3) and (4), we get

$$\Gamma_t = \Gamma_v \overline{Cv} = \frac{G_v}{k_v^2} I + \Gamma_v C_v^0 .$$
⁽⁵⁾

We can therefore write A_t and B_t as

$$A_t = \frac{G_v}{k_v^2} \text{ and } B_t = \Gamma_v C_v^0 .$$
(6)

As discussed above, the crystallite size d is independent of the temperature and intensity below 373 K, so that, at least in this temperature range, we can rationalize the fact that A_t is a constant and B_t depends on temperature.

With the units used so far, we find a vacancy production yield $G_v \approx 1.25 \times 10^{-9}$ sm⁻¹ and $B_t \approx 0.11$ $\exp(-0.3/\text{kT})$ s⁻¹. The activation energy of 0.3 eV is very low compared to a diffusion activation energy in FeAl: indeed, according to Ref. 22, the vacancy formation and migration enthalpies are respectively 0.7 and 1.8 eV at.⁻¹. In view of the extremely narrow temperature range covered by our experiments (308-373 K), the activation energy we found is not reliable.

C. Kinetics of disordering under ball milling

One striking feature of the disordering curves at 308 K shown on Fig. 8 is that, at lower intensities, the disordering process is nonmonotonous: the disordering rate first decreases and then increases. Indeed such a behavior can be qualitatively understood from the same simple model as above [Eq. (2)].

Equation (2) can be rewritten in a formal way as

$$\frac{dS}{dt} = -4\Gamma_t \frac{\partial L}{\partial S} , \qquad (7a)$$

with

$$L = -\int_{0}^{S} \{(1-\sigma)^{2} [\gamma + \exp(2\sigma/\tau)] - (1+\sigma)^{2} [\gamma + \exp(-2\sigma/\tau)] \} d\sigma \qquad (7b)$$

and $\tau = T/T_c$.

L is a Lyapunov function for the evolution of S: L always decreases with time since $dL/dt = (\partial L/\partial S)(\partial S/\partial t) = -1/\Gamma_t (dS/dt)^2 \le 0$. The steeper the slope of L, the more rapid the change of S; L is a minimum at locally stable steady states S^* . Indeed $dS/dt|_{S^*}=0$ implies $\partial L/\partial S|_{S^*}=0$ [Eq. 7(a)] and L being a minimum $(\partial^2 L/\partial S^2 > 0)$, a small deviation from the steady-state value S* always decays in amplitude.

As seen in Eq. 7(b), L is a function of the reduced temperature $\tau = T/T_c$ and the forcing parameter $\gamma = \Gamma_h / \Gamma_t$. L(S) is reminiscent of a free energy function although this analogy must be handled with care,¹⁹ as will be seen below. On varying the control parameters (τ, γ) , the shape of L(S) is varied. The shape of L(S) at a given (τ, γ) gives two things: which are the possible locally stable steady values of S [minimum of L(S)] and what are the qualitative features of the kinetics of the evolution of S towards its steady value. Depending on γ and τ , four distinct behaviors are identified and labeled (a)-(d); those labels are used hereafter to describe the shape of L(S) and the corresponding type of kinetics. Moreover, if on varying (τ, γ) , L(S) changes shape, e.g., from (d) to (a), a phase transition will occur, e.g., from the disordered solid solution to an ordered compound.



FIG. 12. Typical shapes of the Lyapunov function L(S) as a function of S and related kinetic paths (S as a function of time) under forcing as computed from Eq. (2) for several values of the control parameters τ and γ . L(S) may achieve only four distinct shapes labeled (a)-(d) (see text).

We have plotted in Fig. 12 the four possible shapes of the Lyapunov function L(S) as a function of S and related kinetic paths under forcing as computed from Eq. (2) with (τ, γ) values chosen in the vicinity of our experiments (Table I).

(i) With the (a) shape [Fig. 12(a)], L(S) exhibits a single stable steady state at S_{steady} ; S = 0 is unstable; on varying $(\tau, \gamma) S_{\text{steady}}$ can be as close as possible to S = 0. The "(a) type" kinetics is then characterized by a smooth disordering of an initially ordered state to S_{steady} , and a reordering of an initially disordered state to S_{steady} .

(ii) With the (b) shape [Fig. 12(b)], L(S) exhibit two locally stable steady states at S = 0 and S_{steady} ; moreover, there is an unstable state S_{unstable} between those two stable states; in this case S_{unstable} is strictly larger than zero $[S_{unstable}=0$ is in fact the case (a)]. Starting from $S < S_{\text{unstable}}$ the system will disorder to S = 0, while starting from $S > S_{unstable}$ the system will evolve toward S_{steady} . However, in this deterministic description in which the fluctuations are neglected, the use of L(S) is inadequate to predict which of the two stable states is the most stable. The use of a stochastic potential as introduced by Bellon and Martin¹⁹ rather than the Lyapunov function [7(b)] is necessary to predict which of the locally stable states is the most stable one. Then the "(b) type" kinetics could be described as follow: a fully ordered state disorders to S_{steady} ; if S_{steady} is a locally stable state the system will escape this configuration after some time; if S_{steady} is the most stable state, it will remain at S_{steady} ; starting from the disordered state (S=0), the system will remain disordered if the latter is the most stable state or evolve to S_{steady} after a while, if so S = 0 is only locally stable.

(iii) With a (c) shape [Fig. 12(c)], S=0 is the only stable state; however, L(S) exhibit a slowing down at S>0. This slowing down of the disordering rate is at the origin of the existence of a shoulder on the "(c) type" kinetics.

(iv) With the (d) shape [Fig. 12(d)], S = 0 is the only stable state of L(S) and the "(d) type" kinetics is characterized by a continuous disordering to S = 0 of an initially ordered state.

We have schematically plotted in a (τ, γ) plane [Fig. 13(a)] the steady states achieved under forcing. The border line between the ordered phase B2 and the disordered one A2, is deduced from the shape of L(S) [Eq. 7(b)]. On varying (τ, γ) the alloy can change from an ordered state (below the border) to a disordered state (above the border). This situation is equivalent to a phase transition between dynamical steady states instead of equilibrium states. This (τ, γ) diagram is the counterpart of a thermodynamical phase diagram with two intensive parameters like, e.g., temperature and pressure. On varying continuously (τ, γ) , L(S) can change from (d) to (a) shape: the transition is second order. Indeed on changing shape from (d) to (a) the dynamical steady-state degree of order can increase continuously from S = 0 to S_{steady} [see above and Fig. 12(a)]. If L(S) changes from (d) to (b) the transition is first order. Indeed on changing shape from (d) to (b) the dynamical steady-state degree of order increases

abruptly from S=0 to S_{steady} [it had to jump over S_{unstable} ; see above and Fig. 12(b)].

The variation of the shape of L(S) on varying (τ, γ) gives the nature of the A2-B2 transition: as discussed in Ref. 18, the transition is second order for $0 < \gamma < 1.37$ [i.e., L(S) always has (a) or (d) type shape] and first order for $\gamma > 1.37$ [i.e., L(S) can exhibit a (c) or (b) type shape]. The reduced transition temperature at $\gamma^*=1.37$ is $\tau^*=0.42$. In the (τ, γ) plane, this latter point is named a tricritical point.¹⁹ When the transition is first order, the border line between the B2 and A2 fields has been computed with the aid of the stochastic potential.¹⁸ One can point out that this last border split the "(b) kinetics" field in two parts as described above.

The four types of kinetic paths revealed by the four distinct shapes of L(S) depicted on Figs. 12(a)-12(d) are expected respectively in the fields labeled (a)-(d), of the



FIG. 13. (a) Schematic location in the (τ, γ) plane of the fields where the four distinct kinetic paths (a)-(d) defined in Fig. 12 are expected (see text). (b) The location of experiments 1-8 (Table I) in the (τ, γ) plane [see (a)]. The boundaries are computed from Eq. (2): (______) border between ordered B2 and disordered A2; (_____) border between (a) and (b) fields; (. . . .) border between (b) and (c) fields; (_____) border between (c) and (d) fields. The full symbols correspond to the experiments for which the observed kinetic path coincides with that expected from Fig. (a). The empty symbols (1 and 7) correspond to the experiments with a kinetic path not expected in that field of the (τ, γ) phase diagram.

 (τ, γ) plane [Fig. 13(a)]. The borders of the latter fields were plotted in Fig. 13(b) as computed from the condition $\partial^2 L / \partial S^2|_{S=0} = 0$, from the (a)-(d) and (a)-(b) boundaries, $\partial L / \partial S|_{S*} = \partial^2 L / \partial S^2|_{S*} = 0$ (with S^* the locally stable state) for the (b)-(c) boundary, and $\partial^2 L / \partial S^2|_{S*} = \partial^3 L / \partial S^3|_{S*} = 0$ for the (c)-(d) boundary.

The fitting procedure described above was applied to experiments 1-8. The reduced temperature τ and the forcing γ deduced from the fit are given in Table I. It turns out, to our surprise, that our milling device precisely operates in the vicinity of the tricritical point. Indeed, all our experiments were performed in the domain $0.3 < \tau < 0.45$ and $0.5 < \gamma < 2.7$. As shown in Fig. 13(b), the kinetic paths observed in experiments 1-8 are of the type expected in the corresponding fields of the (τ, γ) plane. More precisely, as follows.

Experiments 5, 6, and 8 [Figs. 6(a)-6(b)] performed in the lower range of forcing γ and at not too high a reduced temperature yield a smooth decay of S down to a nonzero steady value. This is typical of "(a) type" kinetics [Fig. 12(a)].

Experiment 7 [Fig. 6(b)] performed at (τ, γ) close to the transition line also yields a smooth decay of S down to a nonzero steady value. This behavior is of "(a) type" (one reordering experiment was done, 9 in Table I), while the milling conditions rather correspond to a "(c) type" kinetics. However, it should be noted that the steady-state value of the LRO parameter (0.35) is at the limit of detection by the technique we used. On the other hand, the simple mean-field theory leading to Eq. (2) is certainly a poor approximation for milling conditions like in experiment 7, since they are in the vicinity of the transition line, close to the tricritical point: in this region, fluctuations [which have been neglected in Eq. (2)] play a major role.

Experiments 1 and 2 (Fig. 8) exhibit a "type (b)" kinetic path [Fig. 12(b)], with the disordered state as the most stable steady state. From Figs. 13(a)-13(b), experiments 1 and 2 were indeed performed in the "(b) field"; however, according to Fig. 13(b), the most stable state should be the disordered state for experiment 2, as observed, but an ordered state for experiment 1 at variance of the observation. As above, experiment 1 is performed very close to the transition line.

Experiment 3 (Fig. 8) exhibits the "(c) type" kinetic path as expected in domain (c) [Figs. 13(a)-13(b)].

Experiment 4 (Fig. 8) performed at the highest available γ value yields a smooth decay to a fully disordered state as expected in "(d) field" of Fig. 13(a). Experiment 4 is indeed very close to the boundary between fields "(c)" and "(d)."

As seen, comparing Figs. 13(a) and 13(b) the fields in the (τ, γ) plane where we observe the four distinct kinetic paths (a)-(d), are located with respect to one another as expected from Eq. (2). The exact location of the borderline between the various fields does not, however, strictly correspond to that computed (experiments 7 and 1).

Indeed, Eq. (2) is the simplest mean-field approximation of the underlying model. More advanced approximations and Monte Carlo simulations of the same mod el^{23} show that the various borderlines should be shifted to lower temperatures and lower γ values. Moreover, the model underlying Eq. (2) rests on a homogeneous description of the disordering and ordering kinetics, while the disorder induced by the shearing process is highly localized. Work is underway to include such heterogeneities in the model.²⁴

Despite the very crude way the complex phenomena occurring during ball milling have been simplified to enter the model described by Eq. (2), it seems that this model of "driven alloys" contains the main features for describing the broad variety of kinetic paths toward the steady state.

More complicated and less generic explanations for the occurrence of "type (c)" kinetics could be looked for. In particular a possible coupling between the buildup of the microstructure (which lasts less than 15 h, irrespective of milling conditions below 373 K) and the kinetics of the order-disorder transition might be argued. However, these arguments suggest that if such effects exist they are not the dominant ones.

(i) In "(c) type" kinetics, the transient state may last as long as 45 h (1, Fig. 8), i.e., much longer than the time to stabilize the microstructure.

(ii) In the reordering experiments [17 and 18 Figs. 6(a) and 6(b)], the starting material had been disordered by a milling treatment which stabilized the microstructure prior to the reordering milling treatment.

(iii) The microstructure is almost insensitive to milling conditions, while the order-disorder transition (transition point and kinetics) strongly depends both on milling temperature and intensity.

Based on the above analysis, the steady-state value of the LRO can be plotted as a function of the milling conditions, as shown in Fig. 14. The shift from a secondorder transition (τ =0.41) to a first-order transition (τ =0.34) is quite clear in this representation. Notice that when the transition is first order, hysteresis effects are to be expected: the milling treatment must be long enough for the transient stationary state to be destroyed. The LRO parameter values in such metastable states are



FIG. 14. Steady-state (full symbol) and transient state (empty symbol) values of the long-range order parameter as a function of the forcing parameter. The curves are computed from Eq. (2) at three distinct reduced temperatures.

shown as open symbols on Fig. 14. This is the counterpart for "driven alloys" of superheating or supercooling in classical first-order phase transitions.

It is worth pointing that Soisson *et al.* recently showed that the order-disorder transition in the same $Fe_{50}Al_{50}$ compound also becomes first order, with hysteresis effects, under high-energy 1 MeV electron irradiation.²⁵

V. CONCLUSION

During ball milling in a vibrating frame grinder, the $Fe_{50}A1_{50}$ compound undergoes a rapid microstructural evolution to a nanocrystalline state, with a crystallite size independent of temperature (up to 400 K) and of milling intensity, as defined by Chen *et al.*² (up to 4100 m/s²). Depending on the milling temperature and intensity, the crystallites are either in an ordered state with the B2 structure or disordered as bcc solid solution (A2 phase). In the ordered state, the degree of order reaches a steady-state value which depends in a reversible way both on the temperature and milling intensity: the higher the

- ¹G. Martin and P. Bellon, in *States and Dynamics of Alloy Phase Transformation*, edited by P. E. A. Turchi and A. Gonis (Plenum, New York, 1994), p. 605.
- ²Y. Chen, M. Bibole, R. Le Hazif, and G. Martin, Phys. Rev. B 48, 14 (1993).
- ³D. Galy (unpublished).
- ⁴E. Hellstern, H. J. Fecht, Z. Fu, and W. L. Johnson, J. Mater. Res. 4, 1292 (1989).
- ⁵E. Hellstern, H. J. Fecht, Z. Fu, and W. L. Johnson, J. Appl. Phys. **65**, 305 (1989).
- ⁶L. M. Di, H. Bakker, Y. Tamminga, and F. R. de Boer, Phys. Rev. B **44**, 2444 (1991).
- ⁷L. M. Di, H. Bakker, and F. R. de Boer, Physica B **182**, 91 (1992).
- ⁸Y. S. Cho and C. C. Koch, J. Alloys Compounds **194**, 287 (1993).
- ⁹J. S. C. Jang and C. C. Koch, J. Mater. Res. 5, 498 (1990).
- ¹⁰Y. Seki and W. L. Johnson, in *Solid State Powder Processing*, edited by A. H. Clauer and J. J. deBarbadillo (The Metallurgical Society, Warrendale, PA, 1990), p. 287.
- ¹¹K. Yamada and C. C. Koch, J. Mater. Res. 8, 1317 (1993).
- ¹²Y. D. Dong, W. H. Wang, L. Liu, K. Q. Xiao, S. H. Tong, and Y. Z. He, Mat. Sci. Eng. A **134**, 867 (1991); P. H. Shingu, B. Huang, S. R. Nishitani, and S. Nasu, Proc. JIMIS-5, Suppl. to Trans. JIM **29**, 3 (1988).
- ¹³F. Reynaud, Phys. Status Solidi A 72, 11 (1982).
- ¹⁴P. Pochet (unpublished).

intensity or lower the temperature, the lower the steady degree of order. A unique steady degree of order is achieved either starting from a fully ordered or fully disordered state. On the way to fully disordered state, the degree of order either decreases monotonically or goes through a short-lived transient state: the higher the intensity, the shorter the duration of this state.

Concerning the degree of long-range order, all the above features are accounted for, in a semiquantitative way, by a very simple model of order-disorder transition in driven alloys proposed a few years ago.¹⁹ Together with a recent study of the order-disorder transition in the same alloy under high-energy electron irradiation, the present work gives support to the theory of "driven alloys" developed in the past decade (for a review see Ref. 26).

ACKNOWLEDGMENT

Fruitful discussions with P. Bellon and F. Soisson are gratefully acknowledged.

- ¹⁵P. Pochet, L. Chaffron, and G. Martin, Mater. Sci. Forum 179-181, 91 (1995).
- ¹⁶H. J. Fecht, in *Nanophase Materials*, edited by G. C. Hadjipanagis and R. W. Siegel (Kluwer Academic, Dordrecht, 1994), p. 125.
- ¹⁷J. Eckert, J. C. Holzer, C. E. Krill III, and W. L. Johnson, J. Appl. Phys. **73**, 2794 (1993).
- ¹⁸F. Soisson, P. Bellon, and G. Martin, Phys. Rev. B 46, 11 332 (1992).
- ¹⁹P. Bellon and G. Martin, Phys. Rev. B 39, 2403 (1989).
- ²⁰G. Inden and W. Pepperhoff, Z. Metalkunde. **81**, 770 (1990).
- ²¹P. Bellon and G. Martin, Solid State Phenom. **30-31**, 107 (1993).
- ²²Atomic Defects in Metals, edited by H. Ullmaier, Landolt-Börnstein, New Series, Group III, Vol. 25 (Springer-Verlag, Berlin, 1991).
- ²³E. Salomons, P. Bellon, F. Soisson, and G. Martin, Phys. Rev. B 45, 4582 (1992).
- ²⁴P. Bellon and R. S. Averback, Phys. Rev. Lett. 74, 1819 (1995).
- ²⁵F. Soisson, P. Dubuisson, P. Bellon, and G. Martin, in *Phase Transformations in Materials*, edited by W. C. Johnson, J. M. Howe, D. E. Langhlin, and W. A. Soffa (The Metallurgical Society, Warrendale, PA, 1994), p. 981.
- ²⁶G. Martin, P. Bellon, and F. Soisson, in *Phase Transforma*tions in Materials (Ref. 25), p. 937.



FIG. 1. Instrumented vertical vibrating frame grinder (see text) (Ref. 2).