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Decomposition of Fe_2B by mechanical grinding

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The decomposition of the intermetallic compound Fe_2B into its elemental constituents has been observed by Mössbauer-effect spectroscopy and x-ray diffraction after mechanical grinding in a horizontal vibratory mill for different times. The system evolution can be described in two stages. During the first one the rms strain increases up to about 6% and the Fe_2B mean grain size reduces to approximately 50 nm. By the end of this step the energy accumulated by the compound becomes of the order of its formation enthalpy. During the second stage segregation of iron is observed at almost constant rate while some of the Fe_2B stress is released and its mean crystallite size continues to diminish up to about 4 nm. A simple calculation indicates that for this degree of fragmentation, decomposition becomes energetically favorable. The occurrence of decomposition instead of amorphization is justified on the basis of kinetic arguments. The influence of air contamination of milling atmosphere has been investigated.

INTRODUCTION

The growing interest for obtaining materials in metastable states has lead to the development of several nonequilibrium processing techniques such as evaporation-deposition, splat cooling, melt spinning, laser heating, ion-beam implantation and mixing, etc. Recently, other methods, like mechanical alloying (MA) and mechanical grinding (MG), have begun to play an important role for preparing solid materials in nonequilibrium thermodynamic states.

In MA, the starting state is a mixture of elemental powders or compounds that usually bears a relatively high free-energy content. The external work drives the system to some lower free-energy states achievable within the characteristic time window of the process. On the other hand, MG begins with a unique, normally stable, intermetallic compound. The process involves the increase of the system free energy via the creation and accumulation of point, line, and surface defects, which generate strain and stress. In this manner the system is brought to an unstable state from which it transforms into another, which becomes more stable under the mechanical action. Again, the relative probability for a particular final state should contain two factors, involving stability and accessibility.

An increasing number of publications on MA and MG of metallic systems is concerned with the determination of the conditions under which a particular system in a particular working situation shall or shall not end in an amorphous state. For the Fe-B system (which is known to amorphize by rapid quenching[1] and by ion-beam mixing[2]) there are controversial results. While Schwarz[3] found that mixtures of Fe and B powders could not be mechanically mixed and amorphized, Jing, Calka, and Campbell reported amorphization for mixtures with high B content (≥ 50 at. %), and Suriñach *et al.*[5] for mixtures of composition $Fe_{86}B_{20}$. On the other hand, Shirahata and Nagumo,[6] starting with a mixture containing ferroboron (essentially FeB and Fe_2B, nominal composition $Fe_{41}B_{52}Al_5Si_2$ plus traces of carbon), and carbonyl Fe ($Fe_{96}C_4$), obtained amorphous systems for B contents between 30 and 50 at. %. Although this range coincides with the theoretically predicted one[6] it must be noted that the amount and diversity of other elements was relevant and so it probably was their influence on the final state.

In a preliminary investigation we tried MA amorphization of $Fe_{75}B_{25}$ using alternative mixtures of α-Fe+Fe_2B, and α-Fe+FeB. In the first case, during the course of the experiment a segregation of α-Fe was detected. The segregation of α-Fe could be the result of transformations like $Fe_2B \rightarrow \alpha\text{-}Fe + Fe_zB$ ($z<2$) where the limiting case would be $z=0$. Fe_2B becoming unstable and decomposing into its elements, instead of amorphizing, under mechanical work would appear surprising at first sight, since the amount of energy needed is much larger than the amount required for bringing it into its amorphous state. Furthermore the first process requires long-range atomic transport while the second one does not. In order to elucidate this question we performed the present study of MG of Fe_2B.

EXPERIMENT

Experiment A

Fe_2B powder (99% purity, Atomergic Chemetals Corp.) was ground in a cylindric, 5 ml, chrome steel vial (11.5% Cr), employing 9 mm diam stainless steel balls (13% Cr), under Ar atmosphere. The grinding was performed with a MM 2 Retsch vibrating mixer mill. Although several samples were used to search for appropriate working conditions, the results presented here mainly correspond to two specimens, 1 g each, filed for up to 150 and 600 h, respectively, at a constant frequency of about 30 Hz. The ball to powder mass ratio was about 3. The MG was interrupted after each milling step, to take small

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amounts of sample for x-ray diffraction (XRD) and Mössbauer experiments. After the diffraction analyses, which took about one hour each, the samples were returned to the vial under Ar environment for the next milling step. The fraction of sample used for each Mössbauer experiment (about 50 mg) was discarded. In order to investigate the influence of possible contamination with air we have performed additional experiments.

Experiment B

The vial (opened) containing the Fe_2B powder was kept inside a latex balloon which was connected to a vacuum diffusion system and to the argon gas supply. A higher than atmospheric pressure was always kept inside the argon branch in order to minimize the risk of air intake. Four washings with argon were carried out, each followed by pumping the system down to 10^{-2} mbar. Next, pressure was reduced to 10^{-5} mbar and kept at this value for about two hours. Afterwards, three more argon washings (similar to the first four ones) were performed. The vial was closed in argon at one atmosphere and sealed with a wide and tight latex ribbon without opening the balloon. Then the balloon itself was sealed at three different positions (so as to build a fourfold barrier for air contamination). Ball to powder mass ratio was increased to 20 in order to reduce grinding processing time (94 h).

Experiment C

The procedure was similar to the previous one with the following differences. Initially Fe_2B was located out of the vial (see Fig. 1). Each washing with argon was followed by pumping the system down to 10^{-5} mbar instead of to 10^{-2} mbar. After five washings Fe_2B was annealed under dynamic vacuum (10^{-5} mbar) at 450 °C for 2 h in order to remove air adsorbed on the particles surface. After cooling down, five more washings (similar to the previous ones) were performed. Fe_2B was transported into the vial with the help of a magnet, without opening the system to air. Grinding time was 94 h. Two more experiments were performed for completeness.

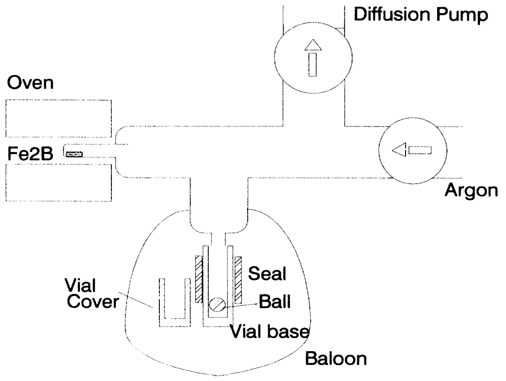

FIG. 1. Arrangement for experiment C.

Experiment D

The sample was encapsulated under argon after several washings in a glovebag. Same quantity of sample and same ball to powder mass ratio as in the other experiments were used. Grinding time was 100 h.

Experiment E

The sample was encapsulated in normal air. Same sample mass and mass ratio were employed. Grinding time was 94 h.

The transmission Mössbauer spectra were obtained with a conventional device, under constant acceleration mode, using a 7 mC ^{57}CoRh source. The velocity scale was calibrated using a 6 μm thick α-Fe absorber. The spectral analysis were performed assuming the existence of quasicontinuous distributions of hyperfine interactions, characteristic of disordered states. In this method each distribution contributing to the Mössbauer spectra was simulated by a large number of subspectra spawning over an appropriate range of hyperfine interaction parameters (hyperfine field, quadrupole splitting, and isomer shift). A linear correlation between pairs of interaction parameters was allowed. The XRD spectra were obtained with the powder method using a PW1140 Philips diffractometer with horizontal goniometer, employing Cu $K\alpha$ radiation.

RESULTS

XRD results obtained after several MG times (experiment A) are shown in Fig. 2. For $t = 0$ h almost all

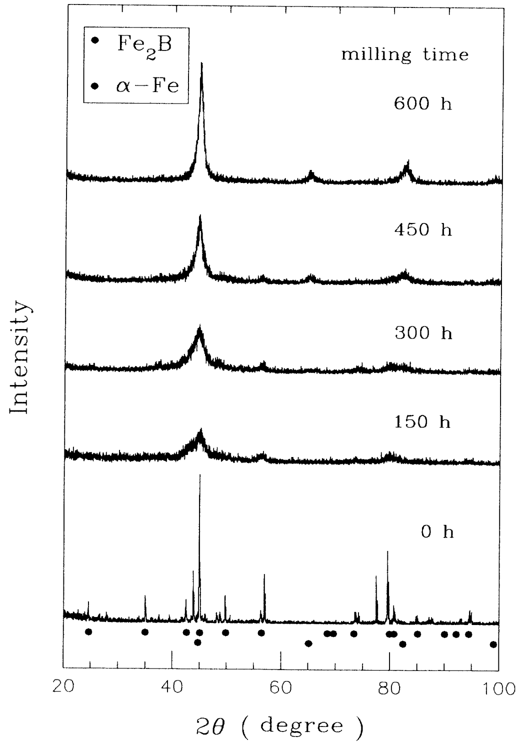

FIG. 2. Cu-$K\alpha$ x-ray diffractograms for different milling times.

diffraction lines corresponded to the tetragonal structure of Fe_2B. A few extra lines were identified as originated from the metastable orthorhombic Fe_2B revealing that a small quantity of this phase was present in the original sample. During the first 150 h, the lines broadened and their height diminished. On further MG, α-Fe diffraction lines appeared and grew while the Fe_2B lines shrinked. After 600 h, almost only α-Fe lines remained. The broadening of the XRD lines is a result of the refinement of microcrystallite size and of the increase of internal strain. The rms strain $\langle \epsilon^2 \rangle^{1/2}$ and the average crystallite size can be estimated applying the method described by Hellstern *et al.*[7] which is based on the fact that broadening deriving from crystallite size is constant in **k** space whereas that due to the lattice internal strain is proportional to k. The results obtained from this analysis are plotted in Fig. 3. The Fe_2B crystallite size decreases with milling time down to a value of about 2–4 nm (200–400 h milling), whereas that of the segregated α-Fe increases from about 3 nm (300 h milling) up to more than 100 nm (600 h milling). In Fe_2B the strain increases rapidly and becomes maximum after 150 h milling. The strain reduction that occurs on further MG suggests that the segregation of α-Fe induces a relaxation of the Fe_2B lattice.

The ^{47}Fe Mössbauer spectra are shown in Fig. 4. The spectra of the original sample and after 150 h of MG were analyzed with a single distribution of magnetic hyperfine (hf) fields centered at $H_{av} \approx 237$ kOe, $\delta_{av} \approx 0.12$ mm/s (see Fig. 5), as expected for Fe_2B. The hf field distribution of the original sample has a little bump at about 270 kOe, which may come from the small amount of Fe_3B detected by XRD. After 150 h the hf field distribution broadened as a consequence of disordering. To give account of the spectrum obtained after 200 h milling a second distribution was needed, with mean hyperfine parameters close to those of α-Fe. The intensity of this distribution increased with further milling at the expense of the one corresponding to Fe_2B. As can be seen in Figs. 4 and 5, from 450 h on α-Fe became the majority phase. From 200 h on the addition of a third interaction corresponding to a small quantity of a paramagnetic phase with cubic symmetry was found to improve substantially the fitting quality. The contribution of this interaction to the Mössbauer spectra showed a slight growing tendency but was bounded to percentages between 2 and 5. Based on its isomer shift we have tentatively identified this paramagnetic phase as small particles of the fcc γ-Fe.

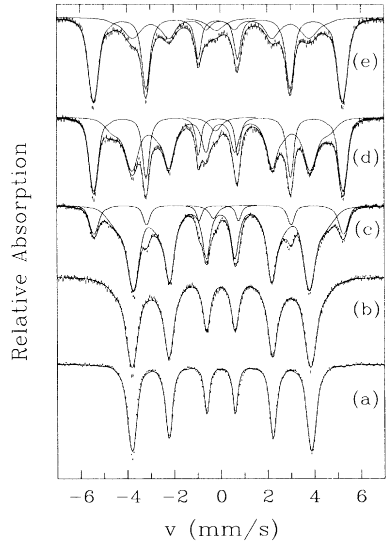

FIG. 4. ^{57}Fe Mössbauer spectra of original sample (a), milled for 150 h (b), 300 h (c), 450 h (d), and 600 h (e), in experiment A.

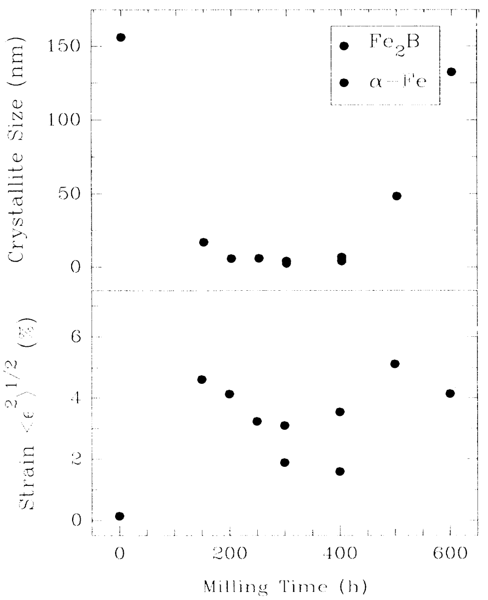

FIG. 3. Crystallite size and rms strain $\langle \epsilon^2 \rangle^{1/2}$ vs milling time as determined from line broadening.

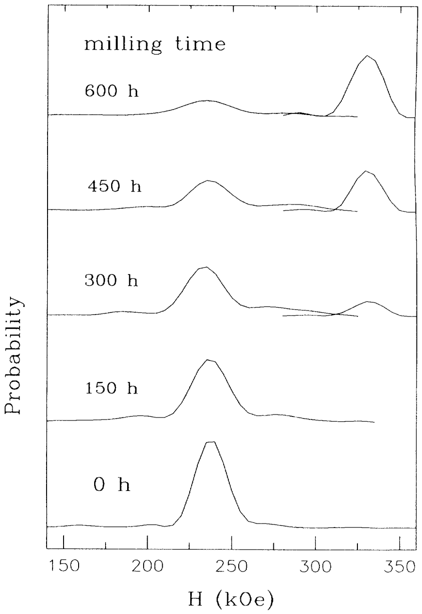

FIG. 5. Magnetic hyperfine field distributions for different times of milling (experiment A).

Figures 6 and 7 show the evolution of the relevant parameters (relative intensity, average isomer shift, hyperfine field, and mean width σ of the hf field distribution) of the main phases α-Fe and Fe_2B. A few particular features in these figures are worth mentioning. (i) The steady evolution of the relative subspectra intensities indicating no sudden change in the transformation mechanism. (ii) The departure of the segregated iron hyperfine parameters from those of α-Fe when detected from the first time (200 h milling). Its reduced hf field and its augmented isomer shift suggest the presence of some amount of boron dissolved in this phase. Only after 350 h milling the isomer shift reached the value expected for α-Fe. (iii) Although the average hf field of Fe_2B increased between 300 and 550 h, the main peak shifted slightly towards lower hf field values, indicating that there is a larger contribution to the spectrum from fields between 260 and 300 kOe. This extra contribution indicates a larger abundance of iron rich phases and it is the origin of the broader hf distribution (σ) observed after these milling times. (iv) Taking into account the previous point, the evolution of σ suggests that the highest disorder of the system occurred after 150 h, in agreement with the strain data (Fig. 3).

The ME and XRD results obtained after milling during 94–100 h in experiments B, C, and D are shown in Fig. 8. The patterns are quite similar to those of Fig. 4(d). However, the results of grinding in air [Fig. 8(E)] are substantially different and indicate that iron environments are dramatically changed.

DISCUSSION

As we have seen the process of MG of Fe_2B can be separated in two stages. First, the Fe_2B becomes disordered as a consequence of strain growth and of grain-size reduction. On further MG the decomposition of Fe_2B proceeds steadily with time without noticeable change in the kinetics. One of the product phases as observed by

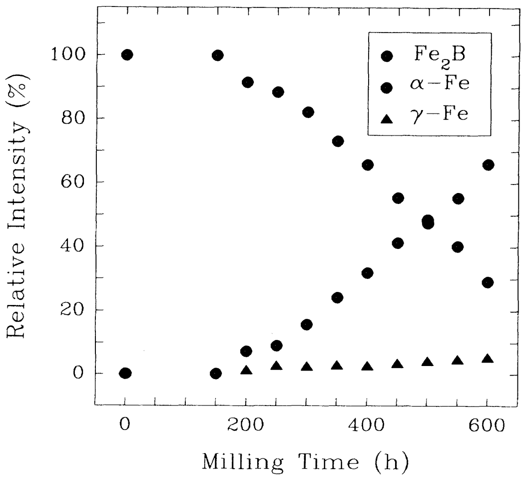

FIG. 6. Relative intensity of the Mössbauer subspectra corresponding to Fe_2B, α-Fe, and γ-Fe as a function of milling time (experiment A).

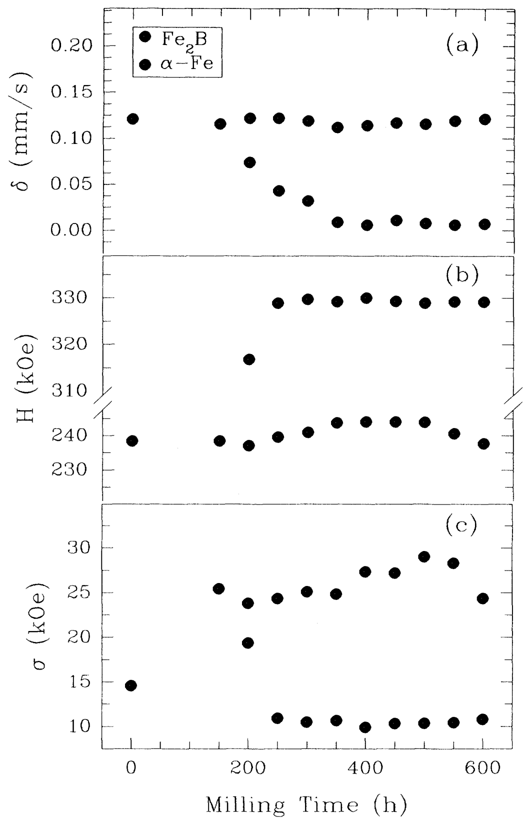

FIG. 7. Room-temperature ^{57}Fe Mössbauer parameters as a function of milling time in experiment A: (a) average isomer shift with respect to α-Fe, (b) average hyperfine field, and (c) rms dispersion of the hyperfine field distribution.

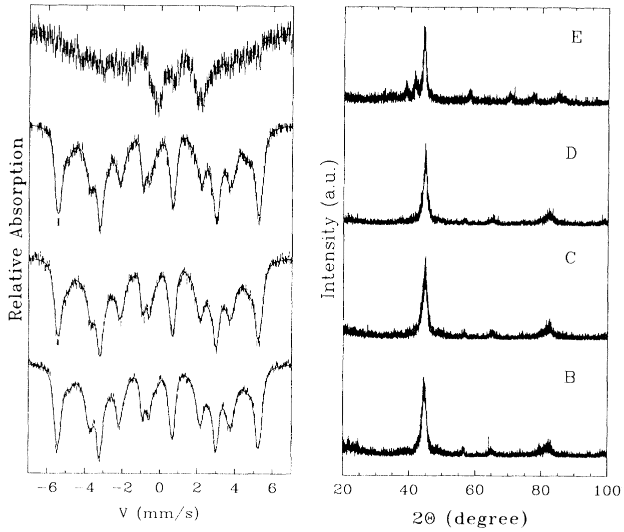

FIG. 8. ME spectra and XRD patterns corresponding to samples obtained in experiments E (closed in normal atmosphere), D (closed in argon in a glovebag), B (closed in argon using a diffusion pump system), and C (closed in argon using a diffusion pump system after degassing for 2 h at 450 °C and $P \approx 10^{-5}$ mbar).

XRD and by Mössbauer effect, is α-Fe. The structure of the hf field distribution indicates the presence of only small quantities of other crystalline or amorphous Fe-B phases.

No other product phase is detected in a quantity comparable with the amount of α-Fe formed. While elemental boron detection is not possible with the techniques available for this investigation, a chemical analysis of the sample ground for 600 h indicated that iron alone cannot account for the totality of the sample.

Balogh *et al.*[9] suggested that decomposition of FeB is driven by oxygen contamination. Possible sources for oxygen in our experiment are the following: (i) presence of oxygen containing compounds in the starting material; (ii) imperfect handling of samples while encapsulating under argon; (iii) imperfect isolation of the vial inner atmosphere; and (iv) oxygen adsorbed onto the original Fe_2B particles (mean size of about 100 μm). Significative amounts of oxygen containing compounds in the starting material should have been detected in our Mössbauer spectra in one of the following three ways: as metallic iron (if boron oxide was developed), as a borate signal, or as iron oxide. None of these situations corresponds to spectrum of Fig. 4(a). In order to investigate on sources (ii)–(iv) we have carried out experiments B, C, D, and E. These four experiments were performed using the same device and under the same experimental conditions, except for the treatment given to the sample before milling and for the atmosphere during milling. Only when the sample was encapsulated in normal air dramatic changes in the ME and XRD results were found. One question we may ask is how much oxygen can induce boron segregation in our milling conditions. For oxygen to be able to retain boron at grain surfaces, a minimum number N_O of O atoms would be needed for a given number N_B of B atoms. For a vial of 5 cm^3 filled with air at atmospheric pressure and containing 0.150 g of Fe_2B, $N_O \approx 5.6 \times 10^{19}$, $N_B \approx 7.3 \times 10^{20}$, and $N_O/N_B \approx 0.08$. These ratio of about one to ten must have been lowered by some orders of magnitude in experiment C, even if desorption was not completely successful. It seems quite safe to assume that such a low oxygen concentration cannot account for the observed results, i.e., oxygen would not be the main factor responsible for Fe_2B decomposition. Since the results of experiment C are alike to those of experiments B and D (see Table I), the reduction of air content in procedure D (or A) is probably enough to turn oxygen influence unnoticeable.

We should try to understand why Yermakov[8] and Balogh *et al.*[9] found that FeB only decomposes when ground in air. To this end new experiments must be done in which the influence of atmosphere is studied keeping other experimental conditions the same. It must be noted that these two groups[8,9] used higher energy devices and longer grinding times for experiments performed in air than for experiments carried out in argon or vacuum.

TABLE I. Percent of ME spectral area corresponding to Fe_2B, α-Fe, and γ-Fe, for samples prepared in experiments B, C, and D (see text).

Experiment	Grinding time (h)	Fe_2B	α-Fe	γ-Fe
D	100	50	48	2
C	94	53	45	2
B	94	54	43	3

At this point at least two questions must be considered. The first one concerns the amount of energy necessary to separate Fe_2B into its components: does the system have the ability to store under MG conditions the 35 kJ/mol needed for this separation? Although this energy is rather high, transformations requiring energies of this order, like the amorphization of PtZr have been accomplished by MG.[10] Energy can be stored by the system in the form of internal stress originated in point defects and dislocations, in new grain boundaries formed by crystallite fragmentation, and also in the form of chemical disorder. After 150 h of milling the Fe_2B phase has a mean crystallite size of about 17 nm (Fig. 3), corresponding to a stored interface energy of only 7.6 kJ/mol (for a grain boundary energy density[15] of 3.07 J/m^2). But the rms strain $\langle \epsilon^2 \rangle^{1/2}$ is 5×10^{-2} (Fig. 3) which amounts for an elastic energy $E \langle \epsilon^2 \rangle /2 \approx 23.8$ kJ/mol (assuming an elasticity modulus $E = 180$ GPa, a typical value for intermetallic compounds[11]). The sum of these two energies is about 31 kJ/mol and hence of the order of the formation enthalpy of Fe_2B, disregarding the energy coming from the creation of new interfaces.

The second question is why does demixing prevail over amorphization which is not only energetically favorable (see Fig. 9) but seems also kinetically favorable (it does not need long-range atomic transport)? Despite this *a priori* statement, the answer may be of kinetic origin. As it was mentioned in the Introduction the Fe-B system can be prepared in the amorphous state by rapid quenching from the liquid, by ion-beam mixing of multilayers Fe/B, by B^+ implantation into iron and by irradiation of pure compounds or mixtures of Fe-B phases. Amorphization of Fe/B multilayer systems cannot be accomplished by

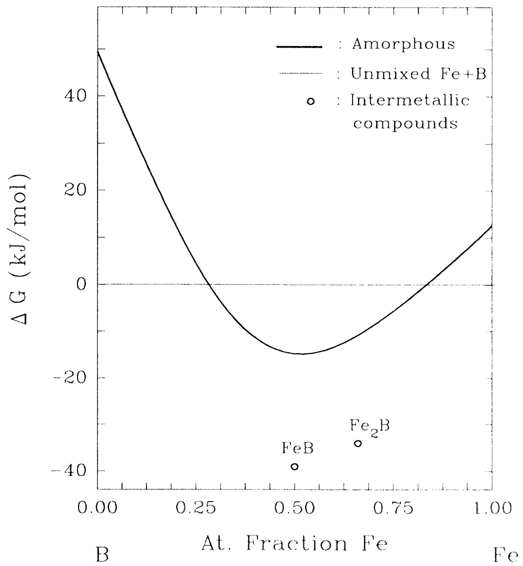

FIG. 9. Free-energy diagram for the Fe-B system.

thermal diffusion only; instead a small increase in resistivity at temperatures between 200 and 300 °C has been observed and interpreted as due to boron diffusion into iron grain boundaries.[2] Under irradiation, amorphization occurs when the number of atomic displacements per atom in the affected region (dpa) overcomes a threshold value. This value is perhaps independent of the projectile employed[12] but it does depend on the target material [dpa$\approx$0.1 for Fe_3B and dpa$\approx$0.3–2.5 for Fe_2B (Ref. 13)]. Although methods for estimating dpa under mechanical treatment are not available, it is reasonable to assume that the density of displaced atoms per impact is sensibly lower than that occurring per incident ion during irradiation. Therefore, the displaced atoms may migrate until they find relative potential energy minima (e.g., at extended defects like grain boundaries) while the crystalline nature of the structure is not critically affected. If the energy minima are reachable within the characteristic time of the process and there is enough asymmetry in the diffusional behavior of both species then spatial separation of boron and iron may proceed by this means. It must be recalled that MG can increase the surface to volume ratio by reducing the grain size. As a matter of fact this happens in our case, according to the evolution of crystallite size shown in Fig. 3. This modification has two consequences. On one hand, the system energy grows due to the surface growth. On the other hand, more diffusing atoms get closer to grain borders.

In studies of thermal boriding of Fe based transition metal alloys, Brackman, Gommers, and Mittemeijer have observed that the process occurs via the formation of one FeB layer (external), and another Fe_2B layer (internal). They found that layer growth is dominated by substitutional boron diffusion which occurs preferentially in the FeB and Fe_2B $\langle 100 \rangle$ directions. Bakker and Di[15] have studied the nature of the disorder created by mechanical action and they have found that it does not differ from that created by other methods; according to their conclusions the type of defects generated is characteristic of the compound. For these reasons we may assume that in our case phase separation occurs by substitutional boron diffusion in Fe_2B toward the grain boundaries. In this way, boron vacancies would accumulate in the interior of the crystallites giving rise to stress which in turn would be finally released by inducing the transformation of the remanent structure into bcc (or fcc) iron.

In order to check whether wetting of the grain boundary with boron leads to a reduction of the surface energy term we have estimated the contributions to the system energy using the model of Miedema.[16] Taking into account that the energy density for a Fe/B phase boundary (3.7 kJ/mol) is lower than the energy densities for Fe/Fe, B/B, and Fe_2B/Fe_2B grain boundaries (37.1, 49.3, and 43.6 kJ/mol, respectively), we have calculated the sum of bulk, free surface, and interface contributions to the enthalpy of a material particle of cubic shape subdivided into small, equally sized, cubic grains, in two cases. (i) A Fe_2B particle constituted by Fe_2B grains. (ii) A particle with the same number of Fe and B atoms as in case (i), but built up from Fe and B crystallites in such a way that the amount of Fe/B interface is maximized (a particular case of boron wetted iron grains or vice versa). The calculation performed as a function of grain size for a 1 μm particle (Fig. 10), indicates that for crystallite size under about 3 nm the separation into Fe and B grains becomes favorable. This result is consistent with the XRD results from which a Fe_2B grain size of about 4 nm has been deduced for MG times form 200 h on.

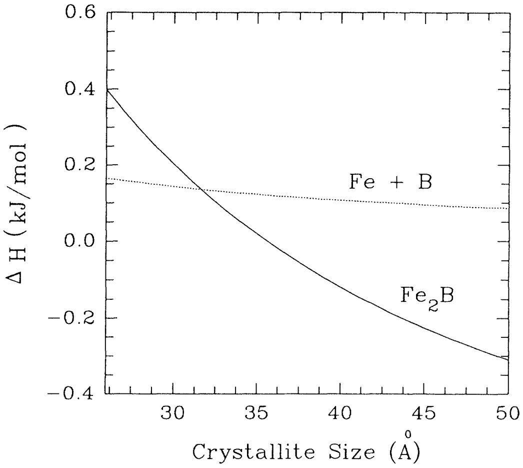

FIG. 10. Comparison of the sum of bulk, free surface, and interface enthalpies calculated for a particle uniformly subdivided into small cubic grains made up of Fe_2B grains or composed by iron and boron crystallites, as a function of grain size.

CONCLUSIONS

We may summarize the effect of milling of Fe_2B by

$$Fe_2B \rightarrow d\text{-}Fe_2B \rightarrow d\text{-}Fe_2B + \alpha\text{-}Fe + (Fe_yB) + B \rightarrow \alpha\text{-}Fe + B ,$$

where d-Fe_2B stands for "disordered" Fe_2B. The accumulation of strain raises Fe_2B energy at levels comparable with the energy of the Fe+B system, even at milling times (150 h) where the interface and surface energy contributions are not very important. On further MG, separation of Fe and B from Fe_2B begins due to stochastic atomic motions while shrinking of Fe_2B grains continues. Once small grains of Fe and B have formed, the recombination of these into small Fe_2B crystallites appears energetically unfavorable. The reason why the system separates into its components instead of transforming into the amorphous phase probably has to do with the kinetics of the process, driven by boron diffusion, and with the low density of atoms set in motion under MG. The experiments performed under different environmental conditions let us discard oxygen as the main factor responsible for phase separation.

Finally, it should be mentioned that even under carefully atmosphere controlled conditions, transference of atoms from and to the milling tools cannot be neglected. Although no evidence for Fe_2B decomposition assisted by this mechanism has been found in this work, more experiments designed to study its influence on MG should be performed.

ACKNOWLEDGMENTS

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