

DISORDERING OF FeAl BY MECHANICAL MILLING

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Abstract. Point defect concentrations in milled samples of stoichiometric FeAl were obtained by Mössbauer measurements. Mössbauer spectra consisted of a single absorption dip with broadening attributed to unresolved hyperfine interactions. A local environment model was used to analyze spectra that allowed for defect-induced changes in monopole interactions at Fe probe atoms due to elementary defects in the two nearest atomic shells. It was found that pre-existing vacancies on the Fe sublattice disappear rapidly in the first five minutes of milling, with a corresponding rapid increase in the concentration of antisite-atom pairs. This behavior is very different to that observed in this laboratory for PdIn, using PAC, where vacancies are the principal defect produced. The difference is attributed to a lower energy of ordering for FeAl. A stationary state was observed after 10 minutes of milling, in which the mole fraction of antisite atoms, the average lattice parameter, and the monopole interactions of defect-free probes all ceased to change further. The mole fraction was observed to become stationary at about 10 atomic percent.

Introduction

Mechanical milling of intermetallic compounds produces point defects and lattice disorder. Prolonged milling may lead to disordering or even formation of new, metastable phases. To understand such phenomena from a fundamental point of view it is useful to be able to monitor the types of point defects formed and how their concentrations develop in the course of milling. Previously, we applied a microscopic probe technique, perturbed angular correlation of gamma rays (PAC), to detect point defects produced by milling of PdIn, a highly-ordered compound having the B2, or CsCl, structure.[1] The perfect structure consists of two interpenetrating simple-cubic lattices, with atoms of each type surrounded by eight atoms of the other. Signals were identified with point defects near ^{111}In probes, including Pd-vacancies and In-antisite-atoms in the first atomic shell and In-vacancies in the second shell, via quadrupole interactions at probes induced by nearby defects. Mole fractions of the various defects were derived from signal amplitudes.

For PdIn, the PAC measurements showed that after only five minutes of milling, mole fractions of lattice vacancies had increased up to about 3%, an enormously high concentration, and remained at that level over the next two hours of milling. On the other hand, the mole-fraction of In-antisite atoms increased much more gradually, reaching the level of a few percent only after an hour of milling. This behavior is attributed to a high ordering energy evidenced, for example, by an almost complete lack of quadrupole interactions in well-annealed stoichiometric samples.[2]

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A different situation is presented by FeAl. Here the ordering energy is lower, and the best annealing treatment available, to heat for about a week at 400 C, [3] does not lead to complete ordering. The x-ray measurements of Xiao and Baker [3] indicate that in annealed, stoichiometric FeAl, mole fractions of antisite Fe-atoms on the Al-sublattice (Fe_{Al}) and vacancies on the Fe-sublattice (V_{Fe}) are about 1% and 2.7%. Somewhat higher mole fractions of 1.8 and 3.6%, respectively, were determined by us for stoichiometric FeAl using Mössbauer spectroscopy.[4]

Our previous Mössbauer measurements were made to investigate defect concentrations in seven annealed samples of FeAl having Fe concentrations of 47-53 % (atomic percent). Mössbauer spectra of the samples consisted of a single broadened absorption dip attributed to unresolved hyperfine interactions. The line shape was fitted to obtain defect concentrations using a local environment model that assumed that defects in the nearest two atomic shells would produce hyperfine interactions that appreciably disturb the interactions of defect-free probes. It was further assumed that disturbance of the monopole interaction (line position) would predominate over quadrupole interaction (line splitting). To simplify the fitting in that study, we further assumed that only Fe_{Al} and V_{Fe} defects would be present, in accord with the x-ray results.[3] In addition to determining how the defect concentrations varied with composition, outcomes of the analysis were monopole-interaction shifts due to Fe_{Al} and V_{Fe} defects in the first and second shells of probe atoms on each sublattice (Fe_{Fe} and Fe_{Al}).

In the present work, Mössbauer measurements are made on FeAl samples milled for various times up to 30 minutes, and after 20 hours. Mössbauer line shapes are analyzed using a model that is an extension of the one used in the previous study of the annealed samples. The principal conclusion is that, unlike for PdIn, the (preexisting) vacancy concentration decreases with milling time, and the dominant defect type produced by milling is the antistructure pair (Fe_{Al} and Al_{Fe}).

Experiment

High-purity Fe and Al foils were arc-melted under argon in a small arc-furnace to form about one gram of FeAl having a composition within 0.1 % (atomic percent) of stoichiometry. The sample was annealed under flowing hydrogen gas at 400 C for 5 days, followed by slow cooling to room temperature. To avoid material contamination, milling was carried out under argon in a Spex 8000 attritor-mill using a vial and two balls of WC. The ball-to-sample mass ratio was of the order of 20-100, which should result in high-energy transfer during impacts. Milling was carried out in time-steps, with about 80 mg of milled material removed between steps and used to make a Mössbauer absorber and a specimen for x-ray diffraction analysis. Mössbauer absorbers were made by mixing milled powder with a binder to provide an average area density of about 10 mg/cm² of natural Fe. Transmission Mössbauer spectra were measured at room temperature using a Ranger MS-1200 spectrometer and ⁵⁷Co(Pd) source having an extrapolated linewidth of 0.25 mm/sec.

X-ray diffractograms were measured using a Siemens 5000 diffractometer. No evidence of phases other than B2 was detected except for the sample milled 20 hours, for which sharp lines due WC fragments, apparently spalled off the vial walls, were also detected. Fits of line positions were used to determine how the average lattice parameter changed with milling time. Also, the ratio of intensities of (100) and (110) reflections provided a qualitative indication of the amount of B2 /bcc order, as described below. From line-widths, the effective crystallite size in material milled for about 30 minutes

was determined to be about 10(5) nm, and there was an appreciable increase of line-width with scattering angle that is generally attributed in the literature to lattice strain.

Mössbauer analysis

Spectra were fitted with superpositions of absorption lines calculated according to various local-environment models having the following common assumptions also used in ref. 4: (1) Samples are homogeneous, single-phase B2 material. (2) The monopole interaction (isomer shift) for probe atoms on either sublattice depends on the numbers and types of defects within the nearest two atomic shells. (3) A defect produces a shift in the monopole interaction by an amount depending on the type of defect and its distance from the Fe probe (shell number).. (4) Shifts due to more than one nearby defect are linearly additive. (5) Recoilless fractions for all sites are equal (so that area fractions are proportional to site fractions.) (6) Point defects are uncorrelated in space, so that intensities of the different spectral components can be expressed as binomial probability functions of the mole fractions of defects. (7) Quadrupole interactions may be neglected. (8) Line shapes of discrete lines are adequately approximated by a Lorentzian profile. (9) Resonant self-absorption can be accounted for by a uniform, broadened linewidth for all discrete lines. A further general description of the fitting procedure is given in ref. 4.

There are four possible elementary defects: the antisite atoms, Fe_{Al} and Al_{Fe} and vacancies, V_{Fe} and V_{Al} . There are thus, in all, eight potential defect-induced shifts, four each for the majority Fe_{Fe} and minority Fe_{Al} probes. The study on annealed FeAl already yielded values for shifts due to Fe_{Al} and V_{Fe} defects in the two shells. These were used as starting values for more general fitting models. It was assumed that defects would appear only in combinations of Schottky defects (V_{Fe} plus V_{Al}), triple defects (2V_{Fe} plus Fe_{Al}), or antisite defects (Fe_{Al} plus Al_{Fe}). Laborious efforts were made to determine a consistent set of defect-shifts for spectra of all the milled samples and to determine the concentrations of the three different defect combinations. In the course of these efforts it was necessary to guess at starting values for defect shifts when none were available. We believe that the shifts and defect concentrations presented below are the best ones attainable, although the possibility that a different set of shifts and concentrations might give better fits cannot be excluded. The chi-squared goodness-of-fit parameter was below 1.1 for fits of spectra from 0 to 5 minutes milling time, increasing to about 1.5 for 10 minutes of milling.

Results

Defects and shifts. From the fitting, it appears that V_{Al} defects are not formed during milling. Best values of defect-induced shifts obtained for the other three elementary defects are listed in Table 1. Uncertainties quoted in the table reflect our qualitative estimates and are not statistical fitting uncertainties. The shift values for the Fe_{Al} and V_{Fe} defects are fairly close to values obtained in ref. 4 from the measurements on annealed FeAl samples. For example, shifts determined there for first-shell defects were -0.15(1) for Fe_{Al} and -0.24(5) for V_{Fe} .

Table 1. Monopole interaction shifts due to defects in FeAl

Defects	Shell number	Probe site	Shift (mm/sec)
Fe _{Al}	1	Fe _{Fe}	-0.13(3)
	2	Fe _{Al}	+0.04(6)
Al _{Fe}	1	Fe _{Al}	+0.11(6)
	2	Fe _{Fe}	-0.05(3)
V _{Fe}	1	Fe _{Al}	-0.22(6)
	2	Fe _{Fe}	+0.11(3)

It can be observed that the shift values obtained for Al_{Fe} defects are approximately equal to the negatives of corresponding values for Fe_{Al} defects. This is consistent with a simple approximation in which Fe_{Al} and Al_{Fe} defects are considered to be charge defects of opposite sign.

Defect mole fractions. Fitted mole fractions of triple and antisite defect combinations were summed appropriately to obtain mole fractions of the elementary Fe_{Al}, V_{Fe} and Al_{Fe} defects. These are shown in Fig. 1 for milling times up to 30 minutes. As can be seen, the mole fraction of V_{Fe} is observed to decrease from about 4% to zero over the first five minutes of milling. After that time, there essentially remains only antisite-atom disorder, with equal mole fractions of Fe_{Al} and Al_{Fe} defects. The antisite disorder increases appreciably over the first five minutes of milling and then remains relatively constant at about 12% after milling for 10 minutes.

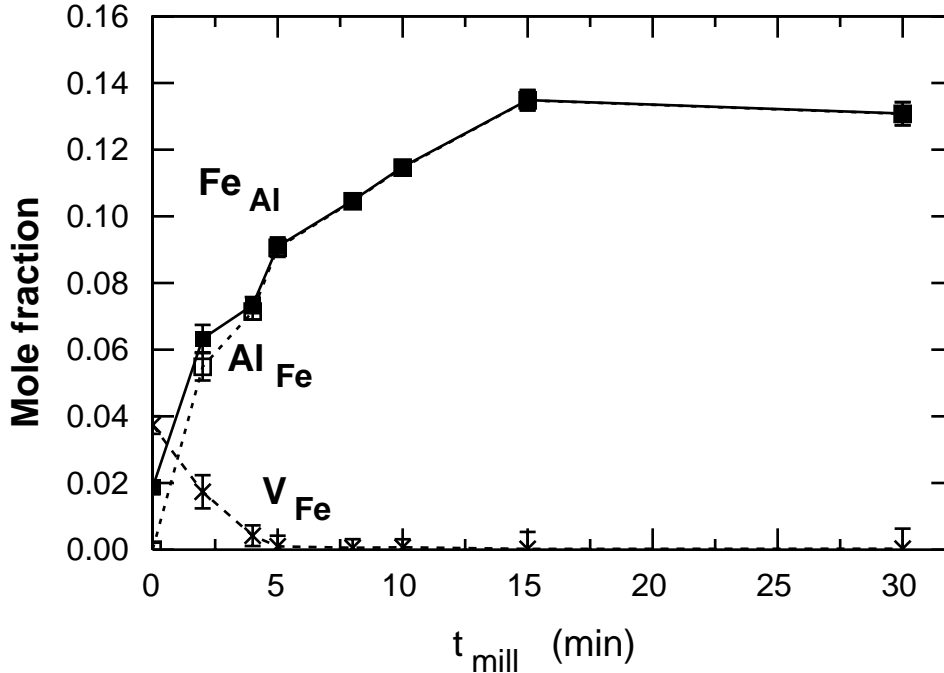


Fig. 1. Mole fractions of defects obtained from fits of Mossbauer spectra.

Monopole interactions of probes without nearby defects. The fitted monopole interactions for Fe_{Fe} and Fe_{Al} probe atoms are exhibited as a function of time in Fig. 2. As can be seen, there is an appreciable change in the interactions during the first 10 minutes of milling, with little change thereafter. The changes are attributed to unresolved shifts from defects in third and further shells.

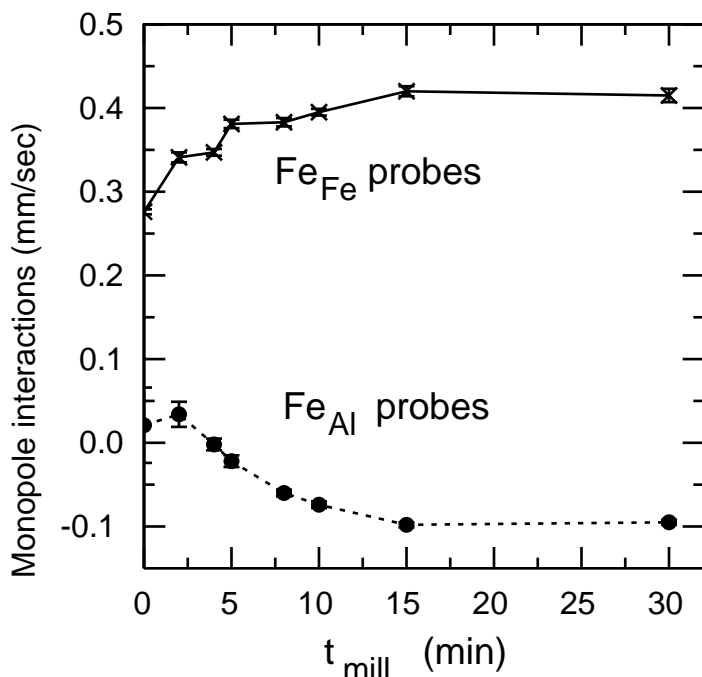


Fig. 2. Monopole-interactions of Fe probe atoms on the Fe and Al sublattices, versus milling time. Shifts are with respect to iron metal.

Lattice parameter changes. The lattice constants of milled FeAl were determined from fitted reflection angles of (110) lines (Fig. 3). As can be seen, the lattice parameter increases by about 0.5% during the first 10 minutes of milling, remaining constant for longer milling times.

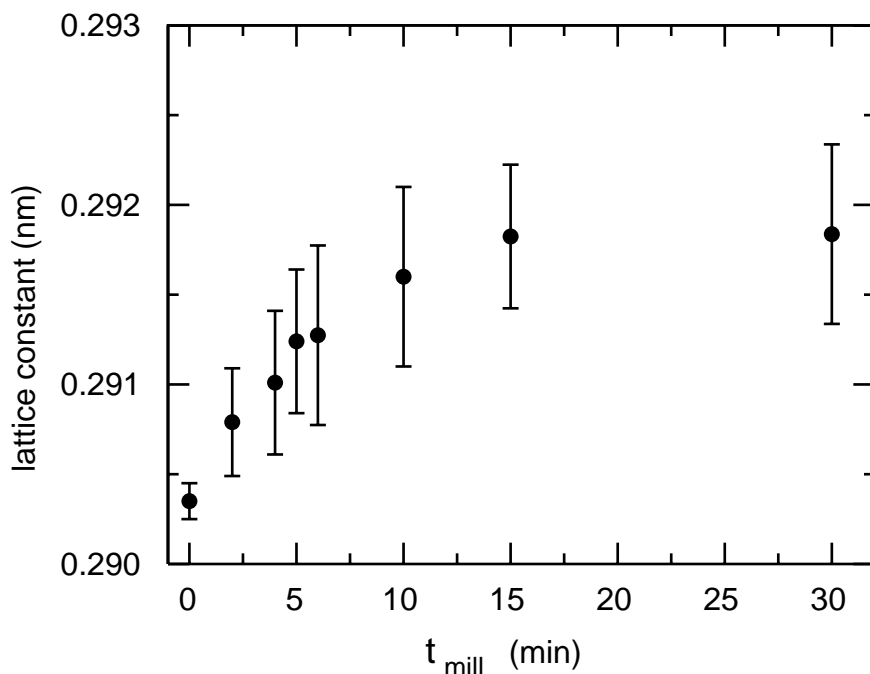


Fig. 3. Lattice constant of FeAl obtained from x-ray measurements after various milling times.

B2/bcc order determined from x-ray intensities. An alternative measure of disorder is provided by the ratio of the intensity of the (100) B2 superlattice line and the (110) bcc reflection. With increasing disorder (of either triple-defect or antisite-atom type) the intensity ratio is expected initially to decrease. Experimental ratios were calculated from fits of the x-ray diffractograms. While the

statistical quality of the x-ray spectra is not very good, the ratio was observed to decrease (not shown) and to stabilize at about 25% of the value at zero milling time for milling times longer than about 5 minutes.

Non-observation of a magnetic signal. FeAl was milled in steel vials in earlier experiments (not shown), after which we observed the milled material to be magnetic by a six-line Zeeman pattern in the Mössbauer spectra having a splitting similar to Fe-metal. Cr contamination was also observed using microprobe analysis. Both effects are attributed to alloying of originally stoichiometric FeAl with steel fragments abrading from vial walls. However, no evidence of a magnetic component was observed in the present Mössbauer spectra (using a WC vial), even after a 20 hours of milling. Therefore the magnetic component observed earlier is attributed to FeAl that has been partially-disordered and enriched in Fe.

Discussion

Defect formation during milling. Antisite-atom pairs are the principal defect formed. From Fig. 1, it is seen that pre-existing V_{Fe} defects disappear in the first five minutes of milling. This can be thought of as being caused by annihilation of vacancies through absorption of Fe defects. After 5 minutes, antisite atoms predominate. The situation is in striking contrast to that of PdIn, for which vacancy production is the dominant process observed in the first few minutes, followed by a very gradual increase in the concentration of antisite defects. We attribute this difference to the higher ordering energy of PdIn, which favors production of defects that do not increase atomic disorder.

Stationary state attained after 10 minutes of milling. As remarkable as are the rapid changes in defect concentrations, monopole interactions and lattice parameters exhibited in Fig. 1-3, the stationary values observed for milling times greater than about 10 minutes are also noteworthy. Most likely, the stationary values indicate that a dynamic equilibrium has been reached between the numbers of defects formed and annihilated. The situation is similar to that for PdIn, for which defect concentrations changed rapidly in the first 5 minutes of milling and slowly thereafter.

Features and limitations of hyperfine interaction methods. Few techniques are available to measure point defect concentrations in milled materials. Hyperfine interaction techniques like PAC and Mössbauer effect have the advantage that they can be used to differentiate among different elementary defects. The major limitation of the present Mössbauer experiments is uncertainty in the analysis of unresolved structure. This problem was less severe in the analysis of spectra of annealed FeAl samples in ref. 4, where fewer defects needed to be considered. In the PAC measurements in ref. 1, resolution was very good. What one needs is a combination of probe and host that provides good signal resolution. The probe must also not be an impurity in order to avoid probe-defect interactions that complicate the analysis of signal amplitudes to obtain defect concentrations. Unfortunately, few good combinations of probes and hosts are available. For the present study, it can not be entirely excluded that a better combination of defect shifts might be found that provides a more consistent analysis. Also, limitations in the methodology, for example ignoring quadrupole interactions, leads to uncertainty. A promising approach that has been applied elsewhere [5] is application of high magnetic fields to Mössbauer samples in order to use magnetic interactions to differentiate among defects in a new way. Steiner et al. [5] made a study of annealed FeAl for the purpose of determining defect concentrations, as in our own study (ref. 4). Like in our study, they attribute signals to defects within

the two nearest atomic shells. However, their method of analysis is different and in some respects more qualitative than our own, so that their results are not directly comparable with ours.

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Note added in proof. Hans Bakker recently noted two rules that are generally obeyed during mechanical-milling of B2 compounds.[6] The first is that the type of disorder introduced by milling is the same as the structural disorder observed in annealed samples on the two sides of stoichiometry. This rule is shown to be violated in the present work since the structural defects include Fe-vacancies, but milling introduces only antisite disorder. The second is that the lattice parameter decreases or increases during milling according to whether vacancy or antisite defects are produced. The increase in lattice parameter in Fig. 3 for FeAl shows that this rule is obeyed.

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