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LETTER TO THE EDITOR

Mechanical milling of Fe–B intermetallics

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Abstract. Mechanical milling of crystalline compounds and mechanical alloying of elemental components yield different products in the case of the Fe–B system. FeB and Fe₂B cannot be amorphized by mechanical grinding. The appearance of the bcc Fe phase during mechanical milling of Fe₂B is due not to decomposition into elemental components, but to contamination from the milling tools. When the stoichiometry is changed, either by contamination during mechanical milling or by mechanical alloying of Fe+FeB or Fe+Fe₂B powder mixture, an amorphous alloy is formed with composition close to Fe₈₀B₂₀.

Solid state amorphization can be realized by a wide range of methods [1]. Mechanical alloying (MA) of elemental powders by ball milling is the most frequently studied process. MA is closely related to diffusion amorphization in multilayers, since it was shown by scanning electron microscopy [2, 3] that the repeated fracture and cold welding of powder particles during milling generates a multilayer structure. Amorphization by grinding crystalline compounds was first reported by Yermakov *et al* [4] for Y–Co compounds and such experiments are now termed as mechanical milling (MM). During MA and solid state amorphization in multilayers the free energy of the system can be reduced by mixing of the elements, but in the case of MM this driving force is absent. The free energy of the crystalline compound is increased by deformation induced defects and chemical disordering [1]. Depending on the relative position of the free energy curves of the different crystalline and amorphous compounds both MA and MM can lead to amorphization, as well as to the formation of nonequilibrium structures besides the stable crystalline compounds [5]. Since both MA and MM are kinetically driven non-equilibrium processes, the different starting states could give different end-products. In spite of these considerations they seemed to yield the same end-products experimentally [5].

Amorphous Fe_{100-x}B_x alloys can be prepared by a variety of methods [6, 7, 8]. The structure of the amorphous phase [9] and the crystallization properties [10] have been extensively studied. On the other hand the experimental results of solid state amorphization are very confusing and not well understood.

While the formation of an amorphous Fe–B alloy by MA is unambiguously demonstrated, the composition ranges and the rates of formation reported [11–14] by different groups are very different. The results are in clear disagreement with thermodynamic calculations [15] which predict a glass formation range for 32–47 at.% B. Since amorphous alloys could be obtained in the predicted concentration range by diffusion amorphization of multilayers [16], the thermodynamic driving force for the amorphization process undoubtedly exists. It is a general observation [17] that the concentration range where the amorphous phase can be formed by solid state diffusion is narrower than the one observed in the case of MA. This is interpreted by deformation induced defects [1] which shift the

free energy of the crystalline solid solutions. It is also assisted by additional factors such as enhanced grain boundary diffusion or atomic scale mixing [17]. This scheme does not seem to work in the case of Fe–B. Though a quite broad concentration distribution (from 20 to 50 at.% B) was shown [18] to exist during the early stage of mechanical alloying, homogeneous amorphous alloy could not be obtained outside the 30–40 at.% B concentration range.

The results on MM are even more surprising. There are two stable intermetallic phases, FeB and Fe₂B. FeB has a high-temperature form, β -FeB, characterized by an orthorhombic structure, with equivalent iron sites giving rise to one well defined set of hyperfine parameters in the Mössbauer spectra. A low-temperature modification (α -FeB) also exists, which was shown to have a CrB (B_F) type structure [19] and a more complicated Mössbauer spectrum [20]. The available experimental results [21, 22] indicate no amorphization of either of the two compounds, but a decomposition process into elemental Fe and B in the case of Fe₂B and into Fe, Fe₂B and B in the case of FeB when long-time millings are applied. For shorter milling times grain size reduction [22] and in the case of FeB a $\beta \rightarrow \alpha$ structural phase transformation [23] are reported.

The aim of this letter is to investigate why the Fe–B system cannot fit into the general scheme concerning the relation between diffusion amorphization, MA and MM. For this purpose MM is investigated more thoroughly since this seemed to produce the most unexpected results.

The mechanical milling was carried out in a vibrating frame single-ball vessel as described elsewhere [18] but with a chrome steel bottom plate instead of the tungsten carbide one.

The phase analysis after milling was performed by Mössbauer spectroscopy. As compared to x-ray diffraction this has the advantage that it is equally sensitive to amorphous and crystalline components. The atomic fraction of the different phases can be estimated with good accuracy from the absorption belonging to the appropriate spectral component. Mössbauer spectra were measured by a conventional constant-acceleration spectrometer and a 25 mCi ⁵⁷Co(Rh) source. The heat treatment was carried out in a Setaram DSC working under Ar atmosphere.

Mössbauer spectra of the FeB and Fe₂B ingots and those of the samples ground for 24 and 48 hours, respectively, are shown in figure 1. FeB shows a $\beta \rightarrow \alpha$ transformation upon 24 hour attrition as reported earlier [23]. Fe₂B mechanically ground for 48 hours clearly shows the spectral features of the crystalline material. Fe₂B has two magnetically inequivalent iron sites giving rise to two sextets with equal isomer shift (0.11 mm s⁻¹ with respect to bcc Fe) but slightly different hyperfine field (24.1 and 23.2 T) and quadrupole splitting (0.11 and 0.01 mm s⁻¹) at room temperature. The spectra of the sample ground for 48 h is best described by a distribution of hyperfine fields with an average value, 22.9 T, slightly lower than that of the ingot and a 2.4 T standard full width. Similar changes were previously interpreted as due to disordering [22], but the formation of a small amount of amorphous fraction cannot be excluded, either.

In the case of longer milling times the appearance of bcc Fe was observed for both compounds, but the milling of Fe₂B was studied more thoroughly. The appearance of bcc Fe was first observed after a 14 day milling time in the case of the Fe₂B sample. In view of the amount of energy necessary to separate Fe₂B into its components (35 kJ mol⁻¹) the assignment of the appearance of bcc Fe to decomposition is highly surprising. This energy far exceeds the energy release ever observed during the recovery and relaxation processes of other nanocrystalline metals and alloys [24] including the nanophase alloy of FeB [23]. However, besides the direct decomposition there are two other possibilities to

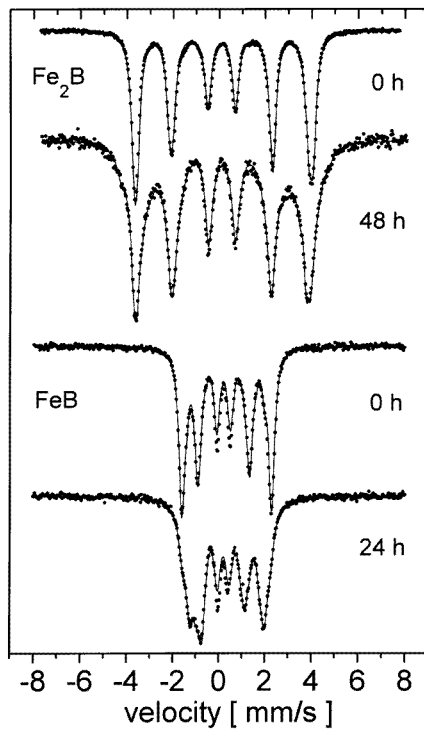


Figure 1. Mössbauer spectra of Fe_2B and FeB ingots and of samples ground for 48 and 24 hours, respectively.

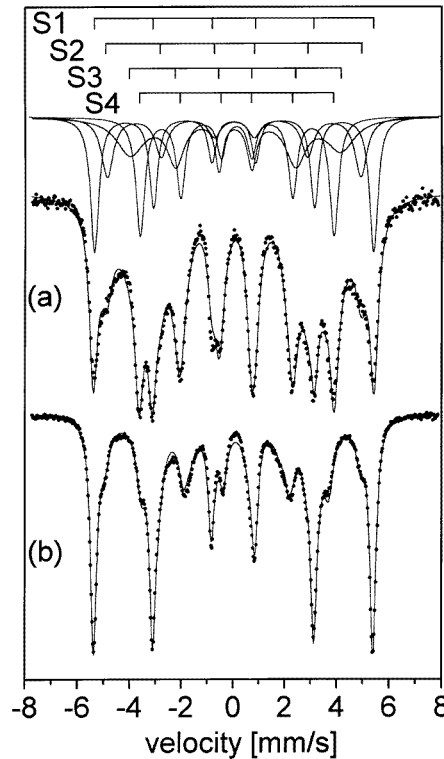


Figure 2. Mössbauer spectra of the sample milled for 21 days (a) and heat treated at 1200 K after the 21 day milling (b). Line positions of bcc Fe (S1), Fe(Cr) solid solution (S2), amorphous $\text{Fe}_{80}\text{B}_{20}$ (S3) and Fe_2B (S4) are indicated and the corresponding subspectra are shown.

explain the appearance of bcc Fe during the milling process: chemical reactions [25] with oxygen under poor vacuum conditions and contamination from the chrome steel milling tools. Due to the increased surface fraction of the powder the first possibility could really play a role in milling under air, but under good vacuum conditions the second possibility is more probable.

The Mössbauer spectrum of the Fe_2B sample mechanically milled for 21 days is shown in figure 2(a). Besides the sextets belonging to bcc Fe and Fe_2B there are two additional sextets. The one indicated by S3 in figure 2 has very broad lines and because of this it appears as an increased background behind the sharp bcc Fe and Fe_2B lines, but it gives about 30% of the total absorption. The other sextet appears as a shoulder of the bcc Fe lines (S2 in figure 2). Since the hyperfine parameters agree with those of Fe atoms in the neighbourhood of Cr impurities, we regard this as a clear sign that the appearance of bcc Fe is due to contamination from the milling tools.

To further check this idea the sample milled for 21 days was heat treated up to 1200 K and a control sample consisting of micrometre size boron and iron powder was mixed together and heat treated the same way. The control sample transformed almost perfectly to Fe_2B with 80% of the iron atoms belonging to this structure. On the other hand, Mössbauer

spectra of the heat treated MM sample can be seen in figure 2(b). Two important changes are to be observed.

- (i) The intensity of the bcc Fe peaks is significantly increased instead of the decrease that would be expected if segregated boron due to decomposition were present.
- (ii) The sextet indicated by S3 has disappeared.

From the ratio of bcc Fe and Fe₂B in the Mössbauer spectra of the heat treated MM probe we estimate that the composition has shifted to Fe₈₄B₁₆ during the milling. The shoulder of the bcc Fe lines is still present after the heat treatment and according to the hyperfine parameters (magnetic splitting, 30.6 T; isomer shift, -0.03 mm s^{-1}) it is due to about 3 at.% Cr in the bcc solid solution [26]. Both the iron enrichment and the Cr content of the sample was directly confirmed by atomic absorption spectroscopy chemical analysis, as well, indicating 74 at.% Fe concentration and the presence of 2 at.% Cr. Taking into account the possible systematic errors of both Mössbauer and atomic absorption spectroscopy, the agreement is acceptable. The absence of decomposition into elemental components is also in accordance with the results of our experiments [27] performed by tungsten carbide milling tools.

The disappearance of the component indicated by S3 is accompanied by an increase of the intensity of the bcc Fe and the Fe₂B lines in an approximately equal amount. This way we estimate that the phase decomposed during the heat treatment is amorphous Fe₈₀B₂₀. It is consistent with the observed broad lines of the S3 component. This indicates that though Fe₂B cannot be amorphized by MM, the addition of iron could do the job. To test this idea FeB+Fe and Fe₂B+Fe mixtures were milled under the same conditions as before.

Mössbauer spectra of the FeB+Fe and Fe₂B+Fe powder mixtures milled for 4 days are shown in figure 3. The starting overall compositions were Fe₈₈B₁₂ and Fe₈₀B₂₀ for the two samples, respectively. After subtracting the fitted subspectra of bcc Fe and bcc Fe+Fe₂B for the two samples, respectively, the remaining subspectra are also shown in figure 3. The broad sextets are characteristic of amorphous Fe–B alloys. This component amounts to 40% of the total absorption in the case of the Fe+Fe₂B mixture. This is a definitely higher amorphous fraction than the one achieved by the 21 day milling of Fe₂B. In the case of the Fe+FeB mixture the broad sextet gives already 71% of the total absorption. The hyperfine field distributions determined by the binomial method [28] are also shown in figure 3. The sample prepared from the FeB+Fe mixture has a smaller peak around 10 T, which may be the result of an α -FeB component not subtracted at the beginning of the evaluation procedure. On the other hand both distributions have a maximum around 27 T, which is characteristic of high-Fe-content (around 80 at.%) amorphous alloys. We come to a similar conclusion if the amount of the different spectral components (Fe, Fe₂B and amorphous Fe_{1-x}B_x) is analysed. From the iron fractions in the different phases and from the starting overall concentration 87 and 84 at.% Fe content were determined as the average concentrations belonging to the hyperfine field distributions of figure 3. These values are quite close to the upper limit (88 at.% Fe) of the amorphization range for melt quenched Fe–B alloys.

Though further work is necessary to investigate the relation of MA and multilayer amorphization, MA and MM experiments clearly result in the formation of different phases in the Fe–B system. While amorphous alloy of around 30 at.% B could be obtained [14, 18] by MA, no amorphous phase is formed by MM of Fe₂B.

The Fe–B system exhibits a clear example that mechanical alloying and mechanical milling can yield different end-products. FeB and Fe₂B intermetallic compounds cannot be amorphized by mechanical milling. On the other hand amorphous phase is easily

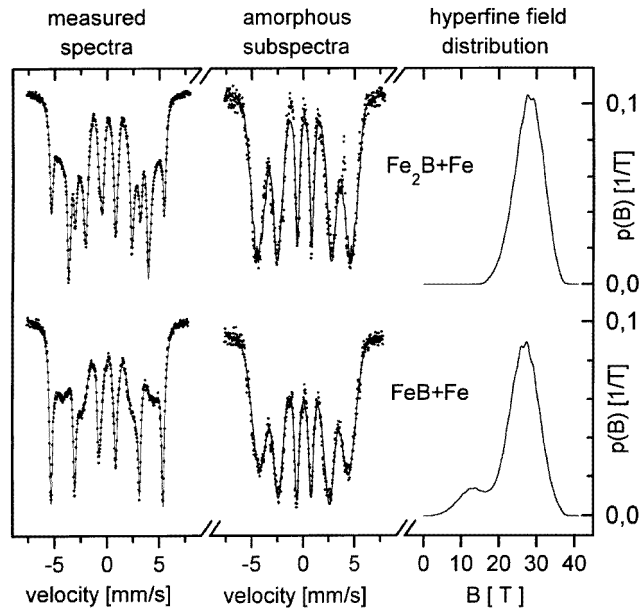


Figure 3. Mössbauer spectra of $\text{Fe}_2\text{B}+\text{Fe}$ ($\text{Fe}_{80}\text{B}_{20}$ overall concentration) and $\text{FeB}+\text{Fe}$ ($\text{Fe}_{88}\text{B}_{12}$ overall concentration) powder mixtures ground for 4 days. The amorphous subspectra are obtained by subtracting the fitted Fe and Fe_2B components from the measured spectra. The hyperfine distributions were evaluated from the amorphous subspectra.

formed when excess Fe is added in the milling process. This shows that chemical disordering plays the most important role in the mechanical amorphization process of this system. In intermetallic compounds chemical bonds usually play an essential role and off-stoichiometry is only allowed in a narrow concentration range. In this way amorphization is significantly promoted by impurities added during the milling process. The question of whether mechanical milling alone is able to amorphize a crystalline material can only be conclusively settled by experiments where the amount and the role of impurities are seriously investigated.

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