Absence of evidence of decomposition of Fe₂B during mechanical grinding

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The appearance of bcc Fe after grinding Fe₂B for a long time has been formerly interpreted as being due to the decomposition of the thermodynamically stable intermetallic compound when the crystallite size is reduced to a few nanometers. The results of our control experiments performed by tungsten-carbide milling tools show that the appearance of bcc Fe has no relation to the grain size but should be connected to contamination when tools made of steel are used to pulverize this material. Mössbauer spectroscopy was applied to search for the appearance of bcc Fe while changes in the grain size were checked by x-ray diffraction and transmission electron microscopy. [S0163-1829(98)09801-4]

INTRODUCTION

A wide range of amorphous alloys can be obtained by high-energy ball milling of elemental powder mixtures or crystalline alloys.[1-3] Free-energy considerations[4] are widely used to predict the composition ranges where the alloy phases formed in the solid-state process are amorphous or partly or fully crystalline. In some cases, however, the observation of a reverse process has been claimed, i.e., when a compound phase decomposes into elemental components[5-8] as a result of milling. In a recent paper the thermodynamically stable intermetallic compound, Fe₂B, was reported[7] to decompose into elemental boron and iron when the crystallite size is reduced to a few nanometers by long-time mechanical pulverization. In view of the amount of energy necessary to separate Fe₂B into its components (35 kJ/mol) this statement is highly surprising. This energy far exceeds the energy release ever observed during the recovery and relaxation processes of other nanocrystalline metals and alloys[9] including the nanophase alloy of FeB.[10] Further questions are raised by the fact that milling of the elemental powder mixture results in the formation of an amorphous alloy.[11,12] Amorphous alloy formation by solid-state diffusion of the elemental components in nanostructured multilayers was also reported.[13]

The decomposition of Fe₂B was deduced from the appearance of bcc-Fe in the x-ray-diffraction pattern and in the Mössbauer spectra, while the segregation of elemental boron was not verified experimentally. However, besides the direct decomposition there are two other possibilities to explain the appearance of bcc-Fe during the milling process: (i) the chemical reaction[14] Fe₂B+O₂→BO₂+2Fe under poor vacuum conditions and (ii) contamination from the chrome steel milling tools.

Although Ref. 7 made serious efforts to exclude the possibility of oxidation (i), the problem of contamination (ii) is not considered.

Though the experimental observation of nanometer-size boron particles would not be an easy task, there is a simple way to check whether the appearance of bcc-Fe is accompanied by boron segregation. In this case iron and boron are just in the right amount to form Fe₂B and after a proper heat treatment the disappearance of bcc-Fe is expected, while in all other cases a change of the overall chemical composition is to be detected. This kind of control indicated a deviation from the Fe₂B stoichiometry[15] for samples ground by chrome steel milling tools and the hypothesis of decomposition was questioned. In this paper we study the possibility of decomposition by presenting milling experiments under circumstances where iron contamination is excluded. For this aim samples have been prepared by tungsten carbide milling tools and characterized by different methods. The grain size reduction was followed by x-ray diffraction (XRD) and transmission electron microscopy (TEM) and the appearance of bcc-Fe was searched by Mössbauer spectroscopy, which is a very sensitive tool to detect a small amount or small grain size bcc-Fe precipitates.

EXPERIMENT

Fe₂B ingots were pulverized in a Fritsch ''Pulverisette 7'' type planetary ball mill supplied with tungsten carbide vials
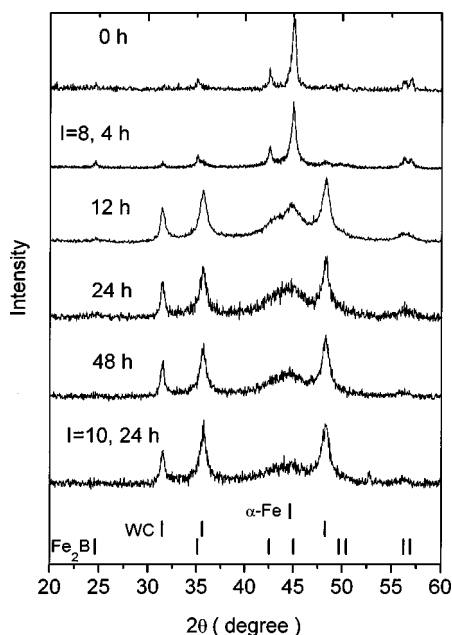
FIG. 1. XRD pattern of Fe_2B pulverized with tungsten carbide milling tools for 0, 4, 12, 24, and 48 h at $I=8$ milling intensity and for 24 h at $I=10$ milling intensity. Line positions of Fe_2B, WC, and bcc-Fe are indicated in the bottom.

and balls. The vials were sealed under argon atmosphere. Eight 4 g balls and ball to powder mass ratio 30 were applied. The milling intensity (I) could be varied on a ten grade scale, where the maximum setting is 700 rev/min. Each time starting with a fresh ingot, milling times from a few hours up to several days were applied.

The XRD measurements were carried out on a Philips EXPERT diffractometer. The spectra from the powder samples were collected in parafocusing geometry, the Cu K_α radiation was selected by a curved pirolitic graphite analyzer placed in the two-θ arm. The powder samples were measured in a Si single-crystal sample holder.

The TEM study of the samples was made with a Philips CM20 electron microscope with TWIN objective lenses and a Noran Voyager energy dispersive spectrometer (EDS) analyzer with HPGe detector. Bright-field and dark-field imaging techniques as well as selected-area electron-diffraction patterns and EDS spectra were used to detect various crystalline phases in the samples. For the specimen preparation a special method based on ion milling[16,17] was used. The powder grains mixed with araldite powder were filled into the slot of a Ti disk in between two small pieces of silicon wafer. The epoxy was then hardened by polymerization in a furnace of 440 K for 1 h. After mechanical grinding to about 50 μm thickness the final thinning was performed by ion milling.

[57]Fe Mössbauer spectra were recorded by a standard constant acceleration spectrometer using 25 mCi [57]Co Rh source and fitted with the usual six-line pattern of Lorenzian line shape.

RESULTS AND DISCUSSION

XRD patterns of the samples milled for different times at two different milling intensities are shown in Fig. 1. Besides the lines of Fe_2B, the pattern of tungsten carbide (WC) ap-

pears already after 4 h milling time at $I=8$. The intensity of the WC lines increases as the milling time is increased and all the well-resolved lines belong to WC when the maximum milling intensity ($I=10$) is applied for 24 h. Broadening of the lines belonging to Fe_2B are already apparent after a 12 h milling at $I=8$. The (002) and (121) reflections at 42.5° and 45.0° angles, well resolved in the unmilled sample, overlap to form a broad asymmetric peak after a one day milling time. This feature is a raw indication that the one day milling at $I=8$ in our experimental setup produced a grain size comparable to the one which was claimed[7] to destabilize Fe_2B. However, since WC has several lines close to those of Fe_2B, the correct evaluation of the average grain size of the Fe_2B crystallites is not easy. A reliable distinction between contributions from grain-size reduction, deformation-induced stress, and amorphous phase formation cannot be made. The average grain size calculated from the line broadening of the (121) peak neglecting other contributions to the line width is about 2 nm in the case of the two samples milled for one and for two days at $I=8$. Further milling results in the gradual disappearance of the distinguishable Fe_2B lines and an amorphouslike broad background is formed under the WC lines as it can be seen in Fig. 1 in case of the one day milling at $I=10$.

To get a more reliable value of the average grain size TEM measurements were made on the samples milled for one and two days at $I=8$. Dark-field TEM micrograph taken with the strongest Fe_2B ring at $d=0.2$ nm of the sample milled for one day is shown in Fig. 2. The TEM micrograph
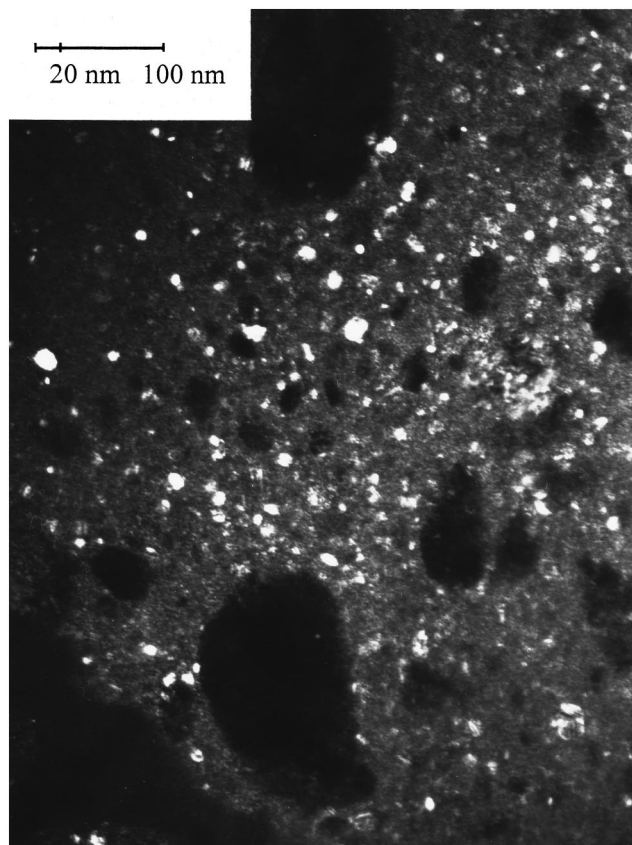

FIG. 2. Electron micrograph of the sample ground for 24 h at $I=8$ milling intensity.
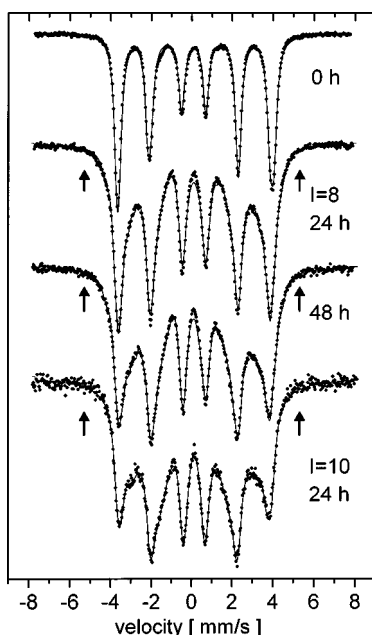
FIG. 3. Mössbauer spectra of the Fe_2B ingot and the samples pulverized by tungsten carbide milling tools for different times at $I=8$ milling intensity and for 24 h at $I=10$. Positions of the two outermost lines of the sextet expected for bcc-Fe are indicated by arrows.

shows large WC particles (dark spots) spread among the smaller Fe_2B crystallites (white spots). The large dark spots are rich in tungsten and the matrix is rich in iron as found by EDS. The diameter of the Fe_2B particles varies between 2 and 20 nm with an average of about 4.5 nm measured manually. This is in reasonable agreement with the x-ray results, and shows that a slight broadening of diffraction lines can come from other than grain-size effects. A similar TEM micrograph was observed on the sample milled for two days. This indicates that no further grain size reduction can be expected and the minimum value is reached at a one day milling time at $I=8$.

Mössbauer spectra of some samples milled for different times are shown in Fig. 3. No bcc-Fe can be observed in any of the measured spectra within a 1 at % accuracy. The spectra can be fitted by two sextets representing Fe_2B (with hyperfine fields of 23 and 24 T and isomer shifts of 0.11 mm/s relative to α-Fe, in good agreement with those of the unmilled ingot) and with additional sextets most probably due to an alloy phase of Fe_2B and WC, which was not aimed to be identified. The atomic fraction of iron atoms in the Fe_2B phase is 52 ± 5 and 37 ± 5 percent of all iron atoms in the samples milled at $I=8$ for one and two days, respectively. According to the TEM picture this fraction has grain sizes in the range of 2–20 nm and one would expect the appearance of bcc-Fe if Fe_2B were destabilized below a 4 nm grain size. One cannot exclude the theoretical possibility that an alloy phase is formed from decomposed elemental Fe and B. In this case, however, the rate of alloying with WC should be equal to or higher than the rate of decomposition. The two rates might have different milling intensity dependence, but

when the $I=10$ milling intensity is applied, no sign of bcc-Fe can be detected either. The amount of the alloy phase increases during further milling and a broad hyperfine field distribution comprises about 80% of the spectra. Since besides the WC lines no sharp peak appears in the XRD pattern, this alloy phase is most probably an amorphous phase formed by solid-state reaction of Fe_2B and WC. It is also obvious that the composition of the sample will be changing gradually with further milling and a steady state of the sample can hardly be attained because of the continuously milled-in wear debris. However, due to the huge mass absorption of W, following the process by Mössbauer spectroscopy becomes increasingly troublesome. A detailed investigation of the milling intensity dependence of the alloying rate of Fe and WC or experiments with milling tools made of different kinds of iron-free materials, e.g., agate or zirconia, should reveal if besides the obviously present contamination effect a hypothetical decomposition process also exists.

CONCLUSION

The notion that intermetallic compounds may decompose to their elemental components when the grain size is reduced below a critical value is widely accepted, though direct tracing of the appearance of both components is usually not very easy[5] and in many cases[6–8] not performed. Therefore chemical reactions (either with the wear debris or with residual gases) or contamination from the milling tools leading to the appearance of one of the elemental components might be misinterpreted. When direct tracing of the appearance of both components is not possible, there are at least two indirect ways to check the decomposition theory. By heat treating the milled sample an increase of the grain size and recovery of the thermodynamically stable intermetallic compound is expected. The other possibility is to follow the process of grain-size reduction by applying milling tools made of different materials. In the case of Fe_2B we performed both kinds of experiments to determine if the appearance of bcc-Fe when the samples are pulverized by Cr-steel tools is a product of decomposition. The first kind of check has shown[15] that the bcc phase contains a significant amount of Cr and does not disappear in heat treatments. Mössbauer spectroscopy, x-ray diffraction, and transmission electron microscopy results reported here show that Fe-based bcc structure does not appear when the Fe_2B compound is milled by WC tools. Though the possibility that the process of decomposition is overwhelmed by an alloying process with the milled in wear debris cannot be unambiguously excluded, the results of the two series of measurements cast serious doubt on the interpretation that Fe_2B is decomposed into elemental components when the grain size is reduced to the nanometer range.

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