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Mechanical alloying of Fe–B

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Abstract. Fe–B alloys in both a nanostructural state and a disordered amorphous-like state have been produced using a novel ball-mill method. Mössbauer measurements at room temperature and 4.2 K on materials of nominal starting compositions Fe₈₀B₂₀ to Fe₄₀B₆₀ combined with x-ray diffraction and differential scanning calorimetry, revealed that samples with low B-content (≤ 34 at. % B) were formed mainly in a nanostructural state while samples with high B-content (≥ 50 at. % B) formed primarily in an amorphous-like state. The detectable B content of the mechanically alloyed samples was found to be lower than the nominal composition for all samples. The presence of unreacted B was confirmed by annealing experiments in which the expected fractions of phases α -Fe, Fe₂B and FeB were obtained as crystallization products. In the samples, which partially exhibit a nanostructural state, B seems to be present only in the disordered interfacial regions.

1. Introduction

Amorphous Fe–B and related alloys exhibit attractive soft magnetic properties. In the main they have been produced by rapid quenching from the melt using ribbon spinning techniques. Applications of such ribbon spun alloys [1] have to some extent been restricted by their shape. Recently, ball-mill technology has been introduced in the preparation of mechanically alloyed amorphous materials although the production of amorphous Fe–B has so far been unsuccessful [2].

A further recent development in materials research has been the preparation of nanocrystalline materials, also known as nanostructures. These materials have very small crystal sizes ranging from about 1–10 nm. Originally, nanocrystalline materials were considered as compact solids with nanometre-sized crystals. In this paper we refer to nanostructures regardless of the degree of compactness. It has been shown that materials having a large proportion of atoms located in the very disordered interfacial regions of polycrystalline materials have various novel physical properties [3]. Nanostructures were first prepared using gas condensation techniques. A review of nanocrystalline materials with details of their synthesis, structure and properties has been published recently by Gleiter [4].

Recently, using a novel ball-mill with sophisticated control of the movements of the balls we prepared samples using start materials in the range Fe₈₀B₂₀ to Fe₄₀B₆₀ and examined them by x-ray diffraction [5]. Mössbauer spectroscopy is highly suitable for

investigation of the phases and structures produced by the mechanical alloying of Fe-based materials [e.g. 6, 7]. In this paper we compare Mössbauer measurements taken at room temperature and at 4.2 K on mechanically alloyed Fe-B alloys with x-ray diffraction and thermal analysis measurements carried out on the same samples.

2. Experiment

Mixtures of elemental iron and boron powders of four nominal compositions (80, 66, 50, 40 at.% Fe) were used as starting materials for the ball milling. The purity of both the Fe and B powders was 99.8% (Johnson Matthey). The mean size of iron particles was $\sim 40 \mu\text{m}$ and that of the boron particles $\sim 60 \mu\text{m}$. For convenience in all of the following discussion, the mechanically alloyed materials are referred to by their nominal starting compositions.

Mechanical alloying was carried out using a novel ball-mill with magnetically controlled movement of a few hardened steel balls [5]. This allows some control of the distribution of the milling energies. It is estimated that any contamination associated with the balls and cell (stainless steel) materials during the milling process is less than 1.5 at.% [5]. The evolution of the structure was monitored by x-ray diffraction using $\text{CoK}\alpha$ radiation. Thermal transformations of the ball-milled powders were studied from room temperature to about 700 °C using a Perkin-Elmer differential scanning calorimeter of type DSC-7. Mössbauer spectroscopy was employed at both room temperature and 4.2 K in the standard transmission mode using a ^{57}Co in Rh source. The spectra were calibrated using a standard α -Fe absorber.

3. Results

3.1. X-ray diffraction

The progress of ball-milling of all samples was monitored every 50 h by x-ray diffraction. As expected, because of the low atomic number of B, the x-ray diffraction patterns of the Fe-B mixtures prior to milling were dominated by the α -Fe peaks. Figure 1 shows the x-ray diffraction patterns taken from the Fe-B mixtures at various stages of ball milling. After 400 h of milling the $\text{Fe}_{80}\text{B}_{20}$ sample showed markedly broadened x-ray peaks associated with the BCC α -Fe structure (figure 1(a)). Further milling up to 600 h did not affect the x-ray diffraction patterns. Applying the Scherrer peak broadening formula a grain size of 6.5 nm was obtained. This corresponds to a nanometre scale structure. The x-ray diffraction pattern for the $\text{Fe}_{66}\text{B}_{34}$ mixture after milling for 400 h (figure 1(b)) also shows a stabilized x-ray pattern with broadened α -Fe peaks. This leads to a grain size of 4.0 nm, again consistent with a nanometre-sized structure.

By comparison, the x-ray diffraction patterns for the mechanically alloyed $\text{Fe}_{50}\text{B}_{50}$ (figure 1(c)) and $\text{Fe}_{40}\text{B}_{60}$ (figure 1(d)) samples indicate that an amorphous structure was developed after milling for 250 h. Further information on the x-ray results, including the effects of annealing the ball-milled samples at 800 °C for several hours, has been reported previously [5]. The thermal analysis and Mössbauer measurements outlined below were carried out on the samples in these final milled states.

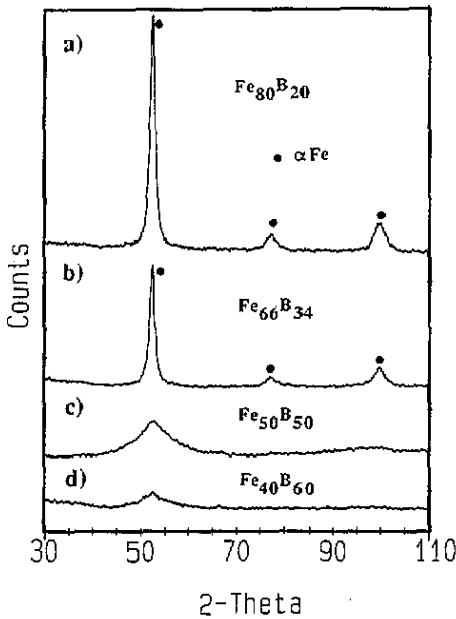


Figure 1. X-ray diffraction of the mechanically alloyed Fe-B samples at various stages of ball-milling. (a) $\text{Fe}_{80}\text{B}_{20}$ after 400 h; (b) $\text{Fe}_{66}\text{B}_{34}$ after 400 h; (c) $\text{Fe}_{50}\text{B}_{50}$ after 250 h; (d) $\text{Fe}_{40}\text{B}_{60}$ after 250 h.

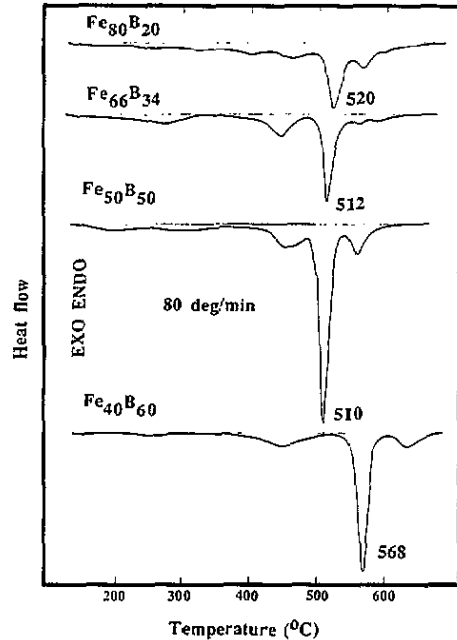


Figure 2. DSC thermograms for the ball-milled Fe-B samples of the nominal starting compositions indicated (heating rate $80^\circ\text{C min}^{-1}$).

3.2. Thermal analysis (DSC)

The crystallization processes of the as-milled samples were studied in detail by differential scanning calorimetry (DSC) using the continuous heating mode at a rate of $80^\circ\text{C min}^{-1}$ (figure 2). For all compositions studied the most dominant feature is the strong exothermic peak occurring in the range $512\text{--}568^\circ\text{C}$. This effect is due to the crystallization of the amorphous phase [8]. It is significant to note that although an amorphous phase is not readily discernible for the ball-milled $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{66}\text{B}_{34}$ alloys by x-ray diffraction (Figures 1(a) and (b)), the existence of an amorphous-like phase in these samples is clearly evident in the DSC data. This means that an amorphous Fe-B phase was produced to at least a partial extent for all of the nominal starting compositions studied in this work. As discussed in section 4 this phase is considered to represent primarily the disordered interfacial phase of ball-milled Fe-B.

The general character of the DSC traces for all compositions is similar: the broad exothermic effect starting at $\sim 100^\circ\text{C}$ and finishing at $\sim 380^\circ\text{C}$ might be due to early surface crystallization (particle surface) [9] and/or internal stress relaxation. The two exothermic peaks occurring on either side of the strong exothermic peak (e.g. the maximum transformations at about $510\text{--}520^\circ\text{C}$ (for $\text{Fe}_{80}\text{B}_{20}$, $\text{Fe}_{66}\text{B}_{34}$ and $\text{Fe}_{50}\text{B}_{50}$) and 568°C (for $\text{Fe}_{40}\text{B}_{60}$)) could be associated with the same crystallization process. Metallic glasses produced by rapid quenching often show multi-stage crystallization processes which can be seen on DSC traces as a series of exothermic peaks [10–14]. Such crystallization behaviour with intermediate stages due to formation of metastable phases

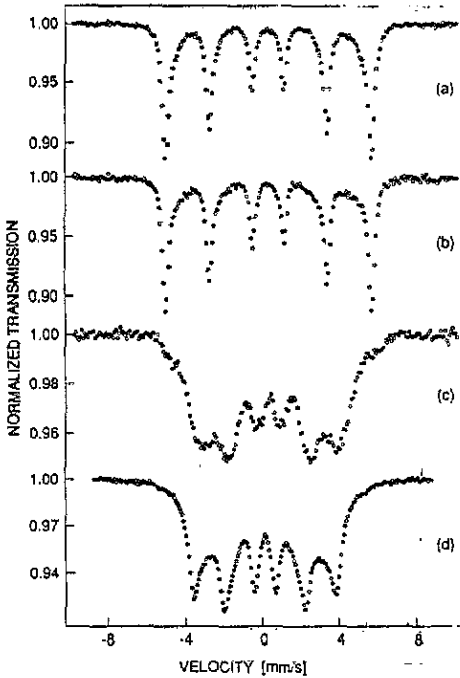


Figure 3. Room temperature Mössbauer spectra of the ball-milled Fe-B samples of nominal starting compositions. (a) $\text{Fe}_{80}\text{B}_{20}$; (b) $\text{Fe}_{66}\text{B}_{34}$; (c) $\text{Fe}_{50}\text{B}_{50}$; (d) $\text{Fe}_{40}\text{B}_{60}$.

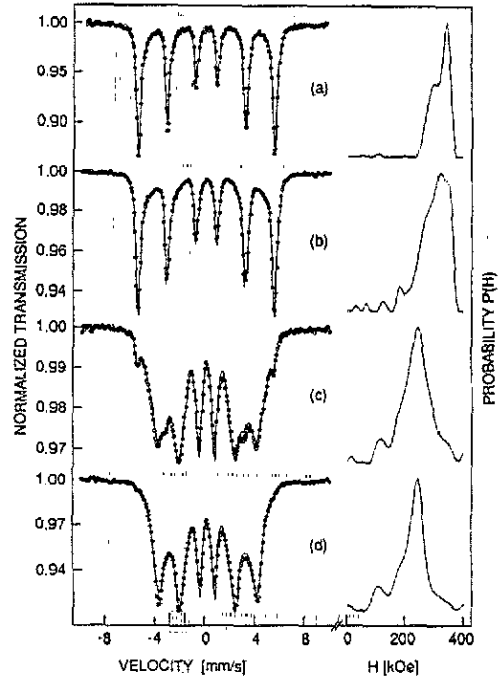


Figure 4. 4.2 K Mössbauer spectra of the ball-milled samples. (a) $\text{Fe}_{80}\text{B}_{20}$; (b) $\text{Fe}_{66}\text{B}_{34}$; (c) $\text{Fe}_{50}\text{B}_{50}$; (d) $\text{Fe}_{40}\text{B}_{60}$. The fits to the spectra were obtained using the program of Le Caër and Dubois [16] with the corresponding probability distributions of magnetic hyperfine fields for the amorphous or interfacial component also shown.

cannot be excluded for ball-milled Fe-B alloys. It could however also be interpreted as a complex crystallization followed by a recrystallization process. Owing to the very fine grain structure it is difficult to investigate details of the crystallization process by x-ray diffractometry. At this stage of the work it is not possible to give a full description of this transformation with further details requiring an electron microscopy study. The recrystallization products have been investigated previously by x-ray diffraction [5].

3.3. Mössbauer spectroscopy

The room temperature Mössbauer spectra for the four milled samples are shown in figure 3. The spectra of the two samples with the lowest B content $\text{Fe}_{80}\text{B}_{20}$ (figure 3(a)) and $\text{Fe}_{66}\text{B}_{34}$ (figure 3(b)) are similar to those obtained from pure nanocrystalline α -Fe [15]. They consist of a sharp sextet pattern superimposed on a broader six-line subspectrum with the combination of the subspectra giving rise to the observed asymmetrical spectra. In agreement with the x-ray diffraction patterns (figure 1(a) and (b)) it is concluded that the ball-milled $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{66}\text{B}_{34}$ samples are predominantly nanostructural. Again, in agreement with the x-ray diffraction and DSC data, the broad lines of the spectra for the $\text{Fe}_{50}\text{B}_{50}$ (figure 3(c)) and $\text{Fe}_{40}\text{B}_{60}$ (figure 3(d)) samples confirm the amorphous state of these ball-milled samples. These spectra, along with their

corresponding distributions of magnetic hyperfine fields, are compared with those obtained for amorphous Fe-B alloys prepared using vapour quenching or ribbon spinning techniques in the following section.

In view of the small particle size resulting from the milling process, effects due to superparamagnetic relaxation may occur in the spectra and make differentiation between structural phases difficult or uncertain. All of the samples were therefore also measured at 4.2 K (figure 4). Other than the expected increases in mean magnetic hyperfine field values for all samples, no significant changes in the shapes of the spectra were observed, consistent with a static distribution of hyperfine fields rather than dynamic fluctuations associated with relaxing magnetic moments. Some additional low intensity sharp peaks can, however, be discerned in the 4.2 K spectrum of the Fe₅₀B₅₀ sample (figure 4(c)). These sharp peaks correspond to the small fraction of unreacted α -Fe remaining in the ball-milled sample. Also shown in figure 4 are the probability distributions of magnetic hyperfine fields derived using the program developed by Le Caër and Dubois [16]. The distributions represent the behaviour of the amorphous or interfacial phase only, with the crystalline Fe component having been stripped away.

4. Discussion

Since the introduction of the ball-milling technique to the study of mechanical alloying and mechanically induced phase transformations, a large number of materials have been produced in the amorphous state [e.g. 17, 6, 7]. So far, however, amorphous Fe-B has not been prepared using this technique [2]. In a conventional ball-mill, the movements of the balls are not controlled and so the energy spectrum during milling is very extended. For a sensitive material such as Fe-B, different regions of the mill energy spectrum may have either constructive or destructive effects in terms of their contributions to the solid-state reaction which leads to the amorphous state. Using the present ball-mill, a narrower range of milling energies can be selected through control of the movements of the balls. The probability of producing an amorphous state appears to have been greatly enhanced by the present ball-milling method.

Amorphous Fe-B alloys produced using either liquid quenching or vapour quenching techniques have been studied extensively. Particularly useful in the present context is the well-established relationship between the average magnetic hyperfine field and the B-content of the samples. Using the hyperfine field data from Chien and Unruh [18] we can estimate the B-content in the amorphous-like Fe-B phase (or the disordered interfacial phases, which we assume to have the same dependence of magnetic hyperfine field on B-content) of the present samples (table 1). Hence, using the relative fraction of the α -Fe and Fe-B phases present in the spectra, as determined from the areas of their subspectra, we can determine the overall B-composition of the mechanically alloyed samples. As shown in table 1, the B-contents in both the amorphous-like phase and overall in the samples, were found to be considerably below the nominal composition of the initial mixture. Also shown in table 1 is the fraction of the amorphous-like phase present in each sample. We therefore conclude that significant fractions of the boron still exist in the elemental form or that B atoms have diffused into the balls and cell material during the milling process. These may be further factors in accounting for the difficulties of obtaining amorphous Fe-B alloys by ball-milling.

In order to check this conclusion that significant fractions of the B remain unreacted, we carried out an annealing experiment on the ball-milled samples. All samples were

Table 1. The mean hyperfine parameters of the amorphous-like or interfacial part of the ball-milled samples as determined from fits to the 4.2 K spectra of figure 4 (H magnetic hyperfine field; is isomer shift with respect to the centre of an α -Fe spectrum; QS quadrupole splitting).

Nominal composition of starting material (at. % B)	Mean hyperfine parameters (4.2 K)			Estimated composition of amorphous-like or interfacial phases (at. % B)	Overall composition of ball-milled samples (at. % B)	Fraction of the ball-milled alloys in the amorphous-like or interfacial phases
	H (kOe)	is (mm s^{-1})	QS (mm s^{-1})			
20	305	0.18	0.00	18	4	20
34	295	0.18	0.02	20	7	35
50	237	0.23	0.01	35	32	95
60	223	0.25	0.01	40	40	100

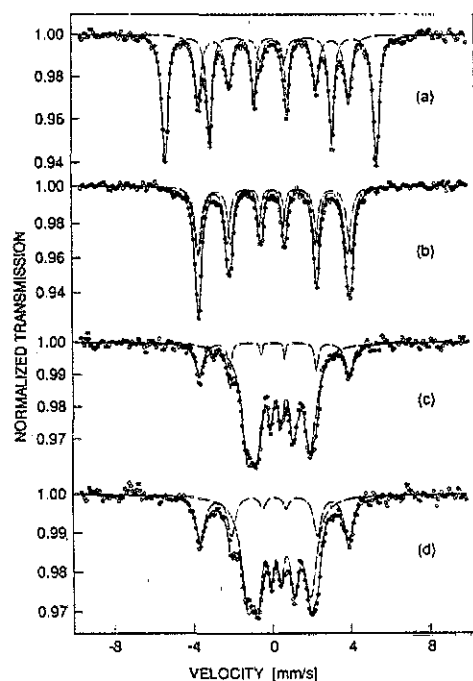


Figure 5. Room temperature Mössbauer spectra of the ball-milled samples following annealing at 800 °C for 0.5 h: (a) $\text{Fe}_{80}\text{B}_{20}$; (b) $\text{Fe}_{66}\text{B}_{34}$; (c) $\text{Fe}_{50}\text{B}_{50}$; (d) $\text{Fe}_{40}\text{B}_{60}$. The fits to the spectra show subspectra associated with: (a) α -Fe and Fe_2B ; (b) Fe_2B ; (c) Fe_2B and FeB ; (d) Fe_2B and FeB as discussed in the text (see also table 2).

annealed at 800 °C for 0.5 h in sealed evacuated quartz tubes. No significant sintering occurred during annealing and the samples were found to be in essentially the same powder form as before. The room temperature Mössbauer spectra of these annealed samples are shown in figure 5. The samples were found to have reacted to give stable phases of α -Fe, Fe_2B and FeB , in general agreement with the x-ray diffraction measurements on annealed samples [5]. The subspectra shown in the fits to the spectra of figure 5 correspond to these phases and good agreement was found with the published spectra and hyperfine parameters for Fe_2B [19] and FeB [20]. Table 2 shows the fractions of these phases present in the annealed samples as determined from the areas of the subspectra. Based on these fractions, the compositions of the samples can be determined

Table 2. The compositions of the samples as estimated from the crystallization products of the ball-milled samples following annealing at 800 °C for 0.5 h. The fractions of phases present were determined from the Mössbauer spectral areas (figure 5).

Nominal composition	Fraction of phases			Composition as estimated from the annealed samples
	α -Fe	Fe ₂ B	FeB	
Fe ₈₀ B ₂₀	0.63	0.37	—	Fe ₈₄ B ₁₆
Fe ₆₆ B ₃₄	—	1.00	—	Fe ₆₆ B ₃₄
Fe ₅₀ B ₅₀	—	0.17	0.83	Fe ₅₂ B ₄₈
Fe ₄₀ B ₆₀	—	0.26	0.74	Fe ₅₄ B ₄₆

as also listed in table 2. These final values are close to the nominal compositions of the start materials (other than Fe₄₀B₆₀ for which only fair agreement is obtained), thus confirming the above conclusion that fractions of the B remain in elemental form in the ball-milled samples even when the Fe was completely consumed during the ball-milling process. The lack of good agreement for the Fe₄₀B₆₀ material is likely to indicate sample inhomogeneity as discussed below.

Comparing the shape of the magnetic hyperfine field distributions of the distributed component of the present ball-milled Fe-B samples (figure 4) with those for amorphous Fe-B produced by rapid quenching [18] reveals significant differences. Whereas, in the latter case, smooth Gaussian-type dominant distributions were obtained, the present ball-milled samples exhibit dominant non-Gaussian distributions as well as several additional features such as low field peaks and pronounced shoulders at the main peaks. This is likely to be related to the relative inhomogeneities in the samples. This indicates the degree of difficulty in obtaining homogeneous material from a mixture of elemental powders by a solid-state reaction due to mechanical alloying. Such inhomogeneities cannot be readily discerned by monitoring the ball-milling process by x-ray diffraction (cf. figure 1; see also [5]), reflecting the suitability of Mössbauer spectroscopy for such investigations.

The mean hyperfine parameters of the distributed components for each of the 4.2 K spectra are given in table 1. Herr *et al* [15] showed that for the Mössbauer spectrum of nanocrystalline pure Fe an interfacial component composed solely of Fe atoms has a larger average magnetic hyperfine field than that obtained in the crystalline α -Fe phase. The present nanostructural samples, however, show that the distributed component has a smaller hyperfine field value than that due to the crystalline component. We therefore conclude that the interfacial components of the present ball-milled samples contain boron atoms. The present materials can therefore be better classified as 'nano-alloy' [21] with atomic alloying occurring only in the interfacial regions between Fe and B nanocrystallites while chemically more or less pure cores of Fe and B are maintained inside the nanocrystallites.

5. Conclusions

Using a sophisticated ball-mill with controlled ball movements we have produced Fe-B alloys in both nanostructural and disordered amorphous-like states. Analysis of the

Mössbauer spectra revealed a boron deficiency in both the overall compositions and in the Fe-B phases of the ball-milled samples compared with the nominal initial compositions ($\text{Fe}_{80}\text{B}_{20}$ to $\text{Fe}_{40}\text{B}_{20}$). That unreacted B was present in the ball-milled materials was confirmed on annealing the samples, thus obtaining fractions of the phases α -Fe, Fe_2B and FeB consistent with the starting compositions. The distributions of magnetic hyperfine fields of the Fe-B phases are found to be different from those of rapidly quenched Fe-B alloys indicating likely chemical or structural inhomogeneities.

Acknowledgments

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