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A study of Fe–B and Fe–Co–B alloy particles produced by reduction with borohydride

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Abstract. Fe–B and Fe–Co–B alloy particles have been prepared by reduction of metal ions in aqueous solution by use of KBH_4 and NaBH_4 . It is shown that the boron content in the particles can be varied by changing the concentration of borohydride and the Fe/Co ratio. For the lowest boron concentrations a mixture of crystalline and amorphous alloys is formed. For higher boron concentrations all the material is amorphous.

1. Introduction

Amorphous alloys are normally manufactured as ribbons [1] or films [2]. The common methods of preparation involve the rapid solidification of molten alloy, so there is frozen-in disorder. These materials have unique properties, which stem from the amorphous structure. They may behave as magnetically soft materials, have high tensile strength, or have enhanced stability against corrosion.

It is well known that the physical properties of amorphous alloys produced from rapid quenching techniques are strongly dependent on the metalloid content [1, 2]. However, the composition of amorphous alloys produced by these methods is in general limited to a range close to the eutectic. This drawback, combined with the fact that the materials are produced as thin ribbons, makes them unsuitable for many engineering applications thereby restricting their development.

In recent years considerable attention has been devoted to the properties of fine alloy particles and their preparation by the reduction of dissolved metal salts using aqueous borohydride [3–15]. It has been shown that Fe–B [10], Fe–Co–B [10–12] and Fe–Ni–B [13] alloy particles produced by this method can be amorphous. These powders have an inherent advantage over ribbons in that they are suitable for use in compaction processes.

In this paper the results of an investigation of the effect of the preparation conditions on the content of boron and the amount of crystalline material in Fe–B and Fe–Co–B alloys are presented.

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2. Experimental details

2.1. Preparation of alloys

The alloys were prepared by the reduction of aqueous solutions of FeSO_4 and CoCl_2 using aqueous solutions of NaBH_4 or KBH_4 . Most reactions were carried out in air, whilst a few were performed in a glove box in an atmosphere of high-purity argon.

Alloy samples that were prepared in air were washed thoroughly with water to remove residual ions from the reaction mixture, and this was followed by washing with acetone to remove the water. Washing was carried out to a Buchner funnel ensuring that at all times the alloy slurry was covered with liquid to prevent direct contact with air. The acetone-wet slurry on filter paper was then transferred to a passivation rig through which a slow flow of argon, with 20–100 ppm of oxygen, was maintained for a period of 24 h. This had the effect of drying the sample and passivating the surface of the particles. Samples that were not passivated were pyrophoric. Mössbauer spectra of the passivated samples showed less than 5% iron in oxides. In fact, elemental analysis of the alloys accounted for 96 to 100% of the mass, in contrast to the results of other authors who reported up to 40 at. % oxygen in their samples [3, 5, 6, 7, 16].

Alloy samples that were prepared in a glove box in an atmosphere of high-purity argon were dried in a flow of argon after being washed with water and acetone. All operations were carried out in the glove box. In this case, depending on the drying procedure, the samples either remained as-prepared or underwent spontaneous annealing [14].

A summary of the preparations is given in table 1. A more detailed description is given below.

Preparations in series A were performed in which the same volume of 1 M NaBH_4 was added rapidly with stirring to a 1 M salt solution of Fe + Co where the Co/(Fe + Co) ratio varied from 0 to 1 in incremental steps of 0.1. This method is similar to that used by Oppegard and co-workers [3] except that in the present experiments the preparations were performed in a glove box under an atmosphere of high-purity argon. The samples were washed with distilled water and acetone under an atmosphere of argon.

Additional series of Fe–B and Fe–Co–B alloys were prepared by dropwise addition of aqueous NaBH_4 of different concentrations, but the same overall quantity of NaBH_4 (from 5 ml of 2 M to 200 ml of 0.05 M), to 250 ml of aqueous solution of FeSO_4 and CoCl_2 . Stirring was maintained throughout. Samples without Co were prepared from 0.04 M aqueous FeSO_4 solutions (series B). Samples containing both iron and cobalt in

Table 1. Details of the sample preparations.

Series A	1 M NaBH_4 added to 1 M salt solution $\text{Fe}_{1-x}\text{Co}_x$ ($x = 0-1$)
Series B	Different concentrations (0.1–1.0 M) of NaBH_4 added to 0.04 M solution of FeSO_4
Series C	Different concentrations (0.05–1.0 M) of NaBH_4 added to 0.2 M overall concentrations of FeSO_4 and CoCl_2 (80% Fe, 20% Co)
Series D	Different concentrations (0.1–2.0 M) of NaBH_4 added to 0.04 M overall concentrations of FeSO_4 and CoCl_2 (50% Fe, 50% Co)
Series E	1 M FeSO_4 solution added to solutions of KBH_4 of different concentrations (0.1–1.0 M)

these series were prepared using aqueous salt solutions in which 20% or 50% of the iron was replaced by cobalt. The overall concentration of the salt solutions was 0.2 M and 0.04 M, respectively (series C and D). In series B and C the influence of the addition time of the reagents was investigated.

A series of Fe–B alloys (series E) was prepared by addition of 10 ml of 1 M FeSO₄ to different concentrations of borohydride whilst maintaining the amount of borohydride constant (i.e. 1000 ml of 0.1 M to 100 ml of 1 M). The salt solution was added dropwise over a period of 15 min with stirring maintained throughout.

The particle size, as estimated by electron microscopy, is in the range 10–200 nm.

2.2. Instrumentation

Mössbauer spectra were measured, at room temperature, using a constant-acceleration spectrometer with a 50 mCi source of ⁵⁷Co in rhodium. The isomer shifts are given relative to α -Fe at room temperature.

The absorption lines in the Mössbauer spectra were fitted to Lorentzian lines employing a least-squares method. The lines for the amorphous alloy components were broad, reflecting a distribution of magnetic hyperfine fields, isomer shifts and quadrupole splittings, and are not true Lorentzian lines. However, fits with broad Lorentzian lines in a sextet gave a reasonable description of the amorphous component. The crystalline components were, likewise, fitted as sextets, but with narrow Lorentzian lines. A doublet, constrained to equal widths and intensities for the two lines, was introduced to account for a small Fe³⁺ oxide component.

The concentration of Fe and Co in the particles was determined by atomic absorption spectroscopy. The boron content was determined by atomic absorption spectroscopy or wet-chemical methods.

3. Results and discussion

3.1. Elemental and structural analysis

3.1.1. Series A. Chemical analysis of the samples from series A shows an increase in boron concentration in the alloys, up to a limit of 30 at.% B, with increasing Co concentration in the aqueous solution (see figure 1). The ratio of Fe to Co in the alloys corresponds closely (generally within 5%) to the ratio in the initial salt solutions.

Mössbauer spectroscopy studies reveal that totally amorphous or a mixture of amorphous and crystalline components are obtained depending on the Co/(Fe + Co) ratio in the solutions. In the absence of Co, the B concentration is 11 at.% (see figure 1) and the sample is predominantly crystalline α -Fe. For Co/(Co + Fe) ratios above 40% the alloys were completely amorphous as seen by Mössbauer spectroscopy. Thus the addition of Co seems to facilitate the formation of an amorphous structure.

3.1.2. Series B. In this series the experiments were carried out with an excess of Fe in solution to prevent severe depletion of the Fe on addition of NaBH₄ solution. The effects of the catalytic breakdown [17] of the borohydride by the small alloy particles are thus reduced. Varying the concentration of Fe in solution from 0.04 to 0.2 M had no observable effect on the boron concentration within the alloy particles. All subsequent experiments were carried out with an Fe concentration of 0.04 M. It was also found that

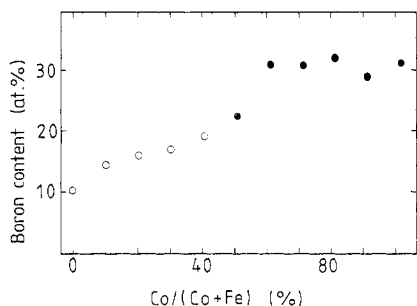


Figure 1. Boron content as a function of the Co/(Co + Fe) ratio in the aqueous solution in series A. Full symbols refer to totally amorphous samples. Open symbols refer to partially crystalline samples.

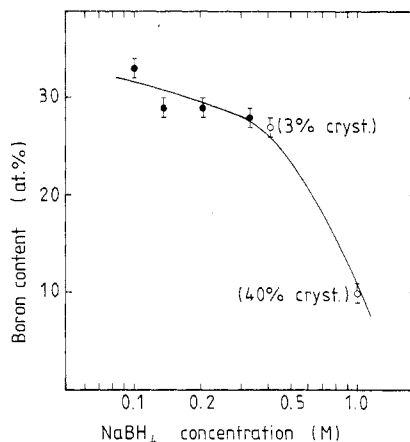


Figure 2. Boron content in the Fe–B alloy particles in series B as a function of the NaBH₄ concentration in the solution. Full symbols refer to totally amorphous samples. Open symbols refer to partially crystalline samples.

variation of the time of addition of borohydride (1 to 8 min) produced no detectable change of the boron concentration in the alloys. This result is expected since each drop of borohydride was added to a solution containing an excess of Fe.

The boron concentrations in the Fe–B alloy was found to increase from 10 to 33 at. % when the borohydride concentration decreased from 1 to 0.1 M (see figure 2).

For the highest concentration of borohydride used the room-temperature Mössbauer spectrum of the passivated alloy showed the presence of both amorphous and crystalline components (see figures 2 and 3). The crystalline component has sharp lines, a magnetic hyperfine field of 33.0 T, zero isomer shift and zero quadrupole splitting, consistent with α -Fe. Least-squares fitting of the spectrum in figure 3(a) shows that 40% of the area corresponds α -Fe. If all boron in this sample is assumed to be present solely in the amorphous alloy, this alloy contains about 17 at. % B. This is probably an upper limit and thus it is not possible to estimate with certainty the lowest concentration of boron necessary to stabilise the amorphous state at room temperature. For melt-spun alloys the amorphous state has been stabilised with as little as 12 at. % B [18]. The hyperfine splitting (27 T) and isomer shift (0.04 mm s⁻¹) of the amorphous component in the spectrum in figure 3(a) are only slightly different from the values of 25.8 T and 0.04 mm s⁻¹ observed for melt-spun samples of Fe₈₃B₁₇ [19].

In changing the borohydride concentration from 1 to 0.4 M, the boron concentration in the alloy increases from 10 to 27 at. % and the crystalline component decreases from 40 to 3% (see figures 2 and 3). The small crystalline component with relative area 3% can be attributed to α -Fe. This crystalline component, although small, is surprising in view of the high overall concentration of B (i.e. 27 at. %), but shows that the boron is somewhat inhomogeneously distributed. For the amorphous component the hyperfine field has dropped from 27 to 24 T and the isomer shift has risen from 0.04 to 0.11 mm s⁻¹, which reflects to the observed large increase in boron concentration in the alloys.

For lower borohydride concentrations (<0.33 M) the boron concentrations are larger than 27 at. % and no crystalline components are present.

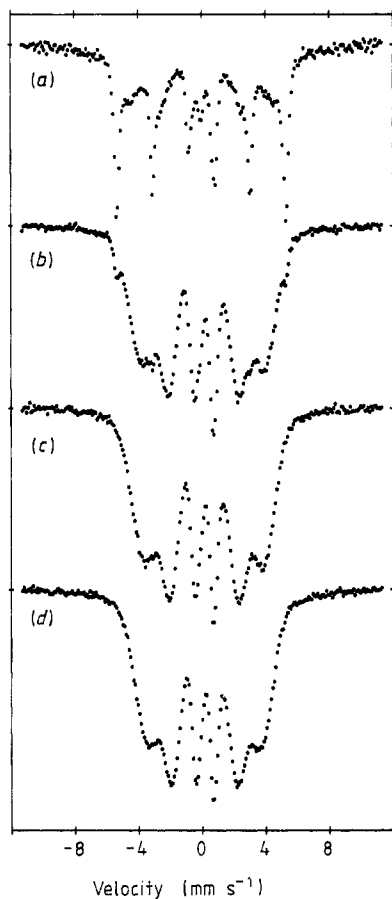


Figure 3. Room-temperature Mössbauer spectra of samples of Fe-B alloy particles from series B prepared with NaBH_4 solutions with the following concentrations: (a) 1, (b) 0.4, (c) 0.2, (d) 0.1 M.

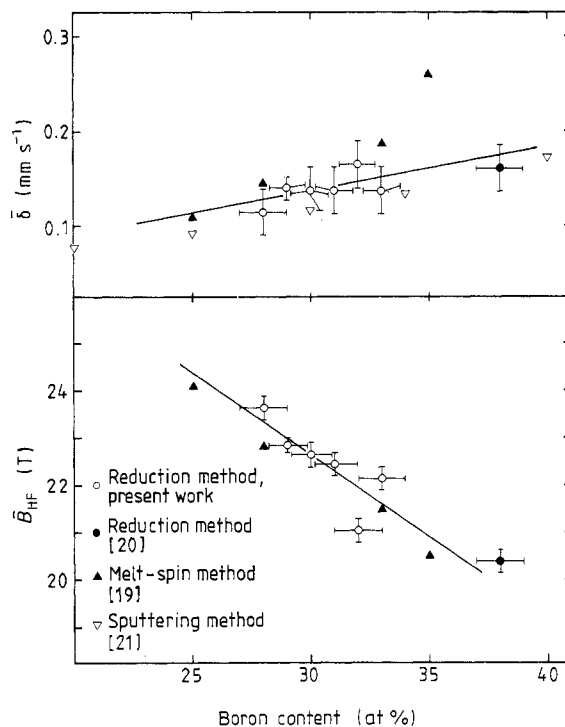


Figure 4. Average magnetic hyperfine fields and isomer shifts of amorphous Fe-B alloys particles (series B) at room temperature. For comparison, results for melt-spun and sputtered alloys are also shown.

In figure 4 the hyperfine fields and isomer shifts have been plotted for amorphous Fe-B alloys prepared by chemical reduction, melt-spin and sputtering techniques.

3.1.3. Series C. It was found that the composition of the alloys in this series was the same within the experimental error when varying the time of addition from 1 to 8 min. The samples described below were prepared by adding the borohydride over a time of a couple of minutes.

Changing the borohydride concentration from 1 to 0.05 M, but maintaining constant the total amount of borohydride added to the salt solution of 0.2 M (80% Fe, 20% Co) produced two effects. Firstly, an increase in boron concentration from 11 to 27 at.% occurred and secondly the $\text{Co}/(\text{Fe} + \text{Co})$ ratio increased from 0.18 to 0.51, compared with a value of 0.2 for the original aqueous salt solution (see figure 5). Further, a completely amorphous structure, i.e. the absence of any crystallinity as observed by Mössbauer spectroscopy (see figure 6), was obtained for borohydride concentrations

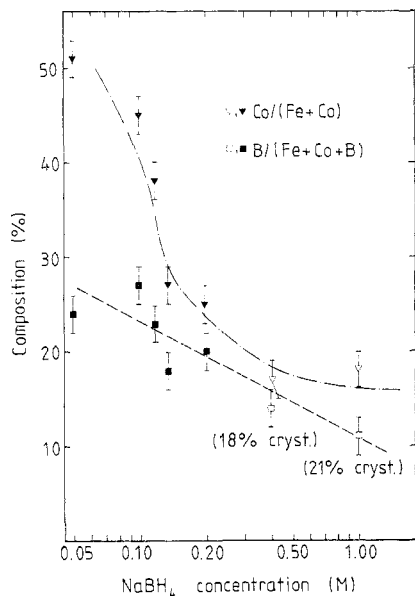


Figure 5. Composition of Fe–Co–B alloy particles from series C (in the original salt solution $\text{Co}/(\text{Fe} + \text{Co}) = 20\%$) as a function of the NaBH_4 concentration in the solution. Full symbols refer to totally amorphous samples. Open symbols refer to partially crystalline samples.

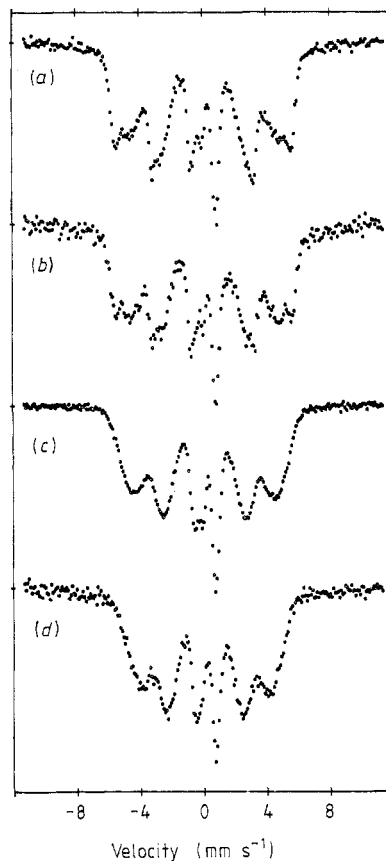


Figure 6. Room-temperature Mössbauer spectra of samples prepared in series C using the following concentrations of NaBH_4 : (a) 1, (b) 0.4, (c) 0.133, (d) 0.118 M.

below 0.2 M and more than 18 at. % B in the alloy. For a borohydride concentration of 0.2 M the $\text{Co}/(\text{Fe} + \text{Co})$ ratio in the alloys is about 0.25. For a borohydride concentration of 0.4 M a crystalline component of 18% is present rising to 21% for a concentration of 1 M.

3.1.4. Series D. In series D experiments, the borohydride concentration was varied from 2 to 0.1 M whilst maintaining the salt solution at 0.04 M (50% Fe, 50% Co). In contrast to the experiments in which $\text{Fe}_{80}\text{Co}_{20}$ salt solutions were used, the boron concentrations remained unchanged at about 27 at. % for all concentrations of borohydride. However, the $\text{Co}/(\text{Fe} + \text{Co})$ ratio changed monotonically from 0.63 to 0.42 with increasing borohydride concentration (see figure 7).

In all cases the alloy samples were amorphous. Mössbauer spectra of these samples are shown in figure 8. The hyperfine fields changed from 22 to 25 T when the $\text{Co}/(\text{Co} + \text{Fe})$ ratio changed from 0.63 to 0.42.

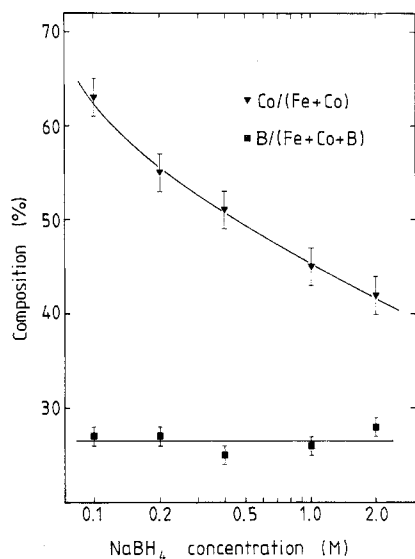


Figure 7. Composition of amorphous Fe-Co-B alloy particles in series D (in the original salt solution the Co/(Fe + Co) = 50%) as a function of the NaBH₄ concentration in the solution.

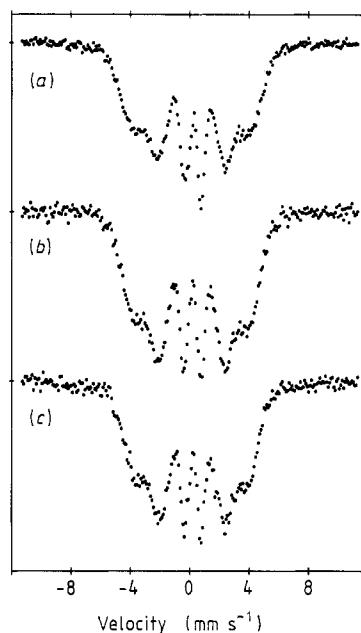


Figure 8. Room-temperature Mössbauer spectra of samples prepared in series D using the following concentrations of NaBH₄: (a) 2, (b) 0.4, (c) 0.2 M.

3.1.5. Series E. In this series the iron salt solutions were added to the borohydride solution.

Small metal and alloy particles are known to catalyse the breakdown of borohydride to the strongly basic metaborate ion [17]. In order to minimise the effect of this catalytic reaction a large excess of borohydride was used in all experiments. The addition of the salt solution to the borohydride results in a vigorous reaction in which the temperature rises which further increases the reaction rate.

In figure 9 is shown the boron content in the alloy particles as a function of the molarity of the borohydride solution. It is seen that this preparation procedure yields a boron content of about 34 at. % for all the borohydride concentrations. Similar boron concentrations are found in Fe-Co-B alloy particles prepared by the same method [10]. All samples in this series were completely amorphous as seen by Mössbauer spectroscopy.

3.2. Comparison with amorphous alloys prepared by rapid-quench techniques

The method of preparation of amorphous alloys described in this paper differs considerably from liquid-quenching and sputtering techniques. It is therefore of great interest to compare the materials prepared by the different techniques. For a given alloy composition many different amorphous structures may in principle exist. When using different preparation techniques the Mössbauer parameters of the samples may therefore be different.

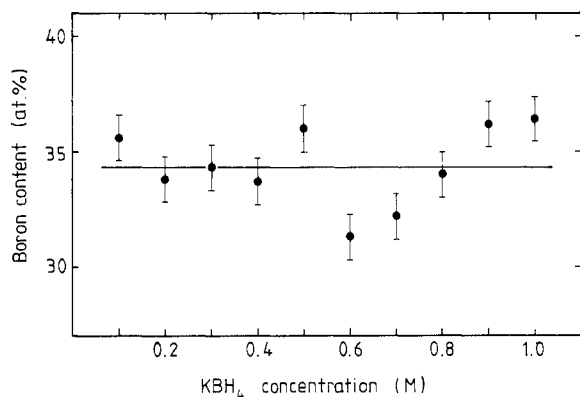


Figure 9. Boron content in the Fe–B alloy particles prepared in series E as a function of the KBH_4 concentration in the solution.

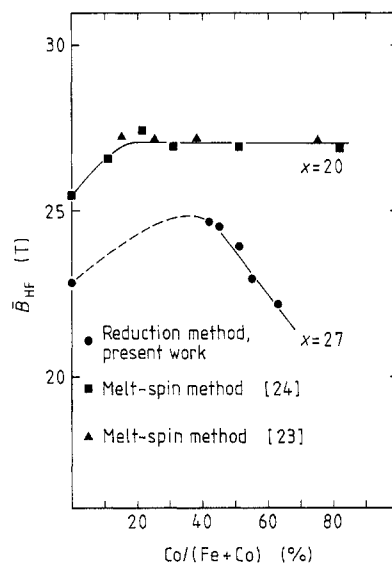


Figure 10. Magnetic hyperfine field, at about 295 K, as a function of the $\text{Co}/(\text{Fe} + \text{Co})$ ratio in amorphous $(\text{Fe}, \text{Co})_{100-x}\text{B}_x$ alloys containing 20 and 27 at. % boron.

For amorphous Fe–B alloys Mössbauer results are available for melt–spun and sputtered alloys with different boron concentrations [19, 22]. The isomer shifts and the magnetic hyperfine fields, at 300 K, for amorphous Fe–B alloys prepared by different methods are compared in figure 4. For the sputtered alloys the magnetic hyperfine fields have only been determined from measurements at 4.2 K and can therefore not be used for direct comparison. Within the experimental error the Mössbauer parameters are identical (except perhaps for the isomer shift of the melt–spun alloy containing 35 at. % boron). The $\text{Fe}_{70}\text{B}_{30}$ sample, prepared by the reduction method, was also studied at 5 K and yielded a magnetic hyperfine field of about 25.3 T, close to that for a sputtered sample with the same composition [22]. The results strongly indicate that the amorphous alloys prepared by the three different techniques have similar structures.

For Fe–Co–B alloys a direct comparison between the melt–spun alloys and the alloys produced by the borohydride reduction can only be made for alloys containing 20 at. % B. We are not aware of other data available for comparison. For the amorphous alloy with composition $\text{Fe}_{60}\text{Co}_{20}\text{B}_{20}$, produced by the borohydride reduction, the magnetic hyperfine field is 27.5 T at room temperature. For the melt–spun alloy of the same composition, the hyperfine field is the same within experimental error [23, 24].

For the other completely amorphous alloys in series C with the compositions $\text{Fe}_{60}\text{Co}_{22}\text{B}_{18}$ ($\text{Co}/(\text{Fe} + \text{Co}) = 0.27$), $\text{Fe}_{48}\text{Co}_{29}\text{B}_{23}$ ($\text{Co}/(\text{Fe} + \text{Co}) = 0.37$), and $\text{Fe}_{40}\text{Co}_{33}\text{B}_{27}$ ($\text{Co}/(\text{Fe} + \text{Co}) = 0.45$) the hyperfine fields are 28, 26 and 23 T, respectively. Because both the ratio of Fe to Co, as well as the boron concentration changes, it is not obvious to what extent each parameter determines the value of the hyperfine field. Although the hyperfine fields for melt–spun alloys with a constant boron concentration (20 at. %), but different Fe/Co ratios, show little change [23, 24] the chemically prepared alloys with 27 at. % B (series D) show significant changes in hyperfine fields for constant

concentration (see figure 10). Similar variations have been observed in alloy particles with 40 at.% B [15]. Samples of Fe-B alloys (series B) indicate that the hyperfine fields depends on the amount of boron incorporated in the alloy which in turn is dependent on the molarity of the borohydride solution.

4. Conclusions

The results of the studies presented in this paper show that it is possible to vary the boron concentration in alloy particles prepared by reduction of Fe and Co ions in aqueous solution by KBH_4 and NaBH_4 .

When the borohydride solution is added to the metal salt solution the boron content in the particles decreases when the borohydride concentration is increased. The boron content in the alloys also increases when the Co/Fe ratio is increased. For a Co/Fe ratio equal to 1:1 in the solution the boron content in the particles is about 27 at.%, essentially independent of the borohydride concentration.

When an iron salt solution is added to the borohydride solution the boron concentration in the particles is about 34 at.%, irrespective of the borohydride concentration.

The alloy particles are partly crystalline and partly amorphous for low contents of boron. For higher concentrations of boron all the material is amorphous.

The Mössbauer parameters for the alloys prepared by the chemical method described in this paper are very similar to parameters observed for alloys of the same composition prepared by the liquid-quench and sputtering techniques, indicating that the structures of the alloys are similar.

Acknowledgments

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