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Chemically prepared amorphous Fe–Ni–B alloy particles

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Amorphous Fe–Ni–B alloy particles have been prepared by chemical reduction of Fe^{2+} and Ni^{2+} in aqueous solution by $NaBH_4$. It was found that within a limited range of $NaBH_4$ concentrations and pH values of the metal salt solution the particles are amorphous. Outside this range the precipitates are partly crystalline. The magnetic hyperfine fields of the amorphous particles, estimated from ^{57}Fe Mössbauer spectroscopy, are similar to those of amorphous ribbons with the same compositions.

1. Introduction

The preparation of amorphous alloy particles by borohydride reduction of transition metal salts in solutions has attracted much attention [1–20]. Such particles may have interesting applications in, for example, magnetic tapes, ferrofluids, catalysts, and they are also interesting because they may be suitable in compacting processes.

The content of boron in the particles significantly affects their properties. It is therefore important to develop preparation techniques by which the boron content can be controlled. By adding an aqueous solution of the metal salts to an aqueous solution of KBH_4 or $NaBH_4$, particles with about 35–40 at % boron can be produced [3, 5, 7, 10]. However, it has been shown [10] that the boron content in particles of Fe–B and Fe–Co–B can be varied by adding $NaBH_4$ solutions of different concentrations to the metal salt solutions. It was later shown that the boron content in Fe–B and Fe–Co–B particles can also be varied by adding solutions of $NaBH_4$ to metal salt solutions with different pH values [15, 16, 20].

In this paper we present an investigation of Fe–Ni–B particles, prepared at different pH of the metal salt solution and different concentrations of the aqueous solutions of $NaBH_4$. A preliminary report on some of the results has been presented elsewhere [19].

2. Experimental procedure

Aqueous solution (200 cm^3) containing $FeSO_4$ (0.16 M) and $NiCl_2$ (0.04 M), i.e. a Fe:Ni ratio of 4 and having a pH of approximately 4, was used for each preparation. Aqueous $NaBH_4$ solution (100 cm^3) of different concentrations (0.10 M, 0.15 M, 0.20 M and 0.25 M) was added dropwise to a vigorously stirred metal salt solution. The $NaBH_4$ solution was added at a rate of about 5 $cm^3\,min^{-1}$. When the pH had reached the desired value it was kept constant (± 0.2) by simultaneous addition of 0.10 M NaOH (for pH > 5.5) or 0.10 M HCl (for pH < 5.5). For the samples prepared at pH 3 the pH was adjusted with a few drops of HCl before $NaBH_4$ addition. Following adjustment of the pH of the metal salt solution, further addition of $NaBH_4$ led to formation of black precipitates. The precipitates were washed in distilled water and acetone. Mössbauer absorbers were prepared from the acetone-wet slurry and immediately frozen in liquid nitrogen in order to avoid oxidation. The remaining material was dried and passivated in a flow of nitrogen gas containing approximately 100 ppm O_2.

The passivated samples were dissolved in acid and the amounts of iron, nickel and boron were determined by atomic and light absorption spectroscopy. The Mössbauer spectra were measured at 80 K using a 50 mCi source of ^{57}Co in rhodium. The isomer shifts are given relative to α-Fe at room temperature. Some of the samples were studied by transmission electron microscopy and electron diffraction using a Philips EM 430 microscope operating at 300 kV and equipped with an energy dispersive X-ray detector. Samples for electron microscopy studies were prepared by comminution of the passivated material in an agate mortar and placing the material on a carbon film placed on top of a copper grid.

3. Results and discussion

Mössbauer spectra, obtained at 80 K, of the precipitates prepared with 0.10 M and 0.20 M solutions of $NaBH_4$ and with different pH values in the salt solution, are shown in Fig. 1. First we discuss the spectra of the samples prepared with an $NaBH_4$ concentration of 0.10 M (Fig. 1a). The sample prepared at pH 3 yields a spectrum which can be fitted with two six-line components. One of these has a magnetic hyperfine field of 34.5 ± 0.5 T, zero quadrupole shift and an isomer shift of $0.12 \pm 0.01\ mm\ s^{-1}$. This component, which constitutes about 65% of the spectral area, can be attributed to crystalline α-Fe, possibly containing small amounts of nickel. The second six-line component with a relative area of about 35%, has very broad lines, an average magnetic hyperfine field of 29 ± 1 T, a negligible quadrupole shift, and an isomer shift of

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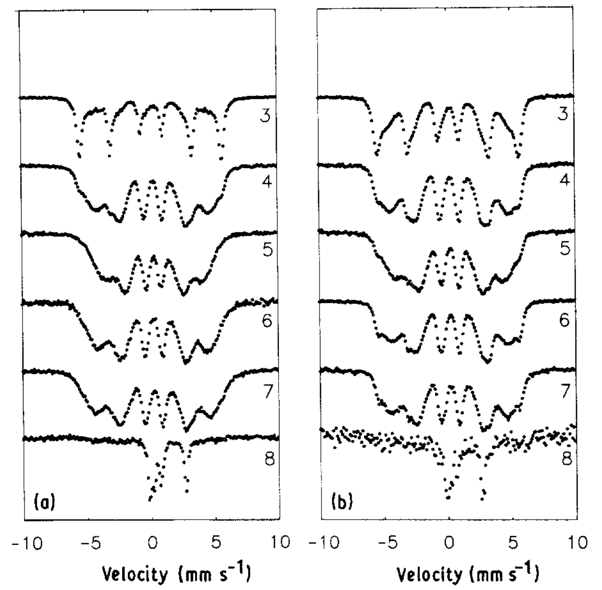

Figure 1 Mössbauer spectra obtained at 80 K for Fe–Ni–B alloy particles prepared by adding aqueous solutions of (a) 0.10 M $NaBH_4$ and (b) 0.20 M $NaBH_4$, to an $Fe_{80}Ni_{20}$ salt solution at the pH values indicated.

0.17 mm s^{-1}. This component can be attributed to an amorphous Fe–Ni–B alloy. In the spectrum of the sample prepared at pH 4, the relative area of the amorphous component has increased to approximately 90%. The remaining spectral area is due to the α-Fe component. For samples prepared in the pH range 5–6.5 only the amorphous component is seen (the detection limit for α-Fe is estimated to be 3–5%). For the samples prepared at pH 8 a completely different spectrum is observed. The relative area of the magnetically split components is very small and the spectrum is dominated by two quadrupole doublets. One of these has a quadrupole splitting of 2.87 mm s^{-1} and an isomer shift of 1.28 mm s^{-1}, whereas the other has a quadrupole splitting of 0.57 mm s^{-1} and an isomer shift of 0.47 mm s^{-1}. These two components can be attributed to paramagnetic Fe^{2+} and Fe^{3+}, respectively [21]. Thus it is seen that the pH value during the reaction is very important for the composition of the precipitates. Only within a limited range of pH values do the precipitates consist of pure amorphous alloy particles. Similar results have been obtained in studies of the preparation of Fe–B and Fe–Co–B alloys [15, 16].

The spectra of the precipitates prepared with an $NaBH_4$ concentration of 0.20 M (Fig. 1b) show the same trend as those of the samples prepared with an $NaBH_4$ concentration of 0.10 M. However, all the spectra in this series contain a component due to α-Fe. The presence of sharp absorption lines due to α-Fe at approximately ± 5.5 mm s^{-1} is clearly seen in all the spectra (except for the particles prepared at pH 8).

The spectra of the precipitates prepared with an $NaBH_4$ concentration of 0.15 M showed that all the iron-containing material is amorphous for pH values between 4 and 7, whereas the samples prepared with an $NaBH_4$ concentration of 0.25 M contained some α-Fe for all pH values between 3 and 7. It thus appears, that only in a certain range of pH values and $NaBH_4$ concentrations the precipitates consist of pure amorphous alloy particles.

Fig. 2 shows the results of the chemical analysis for

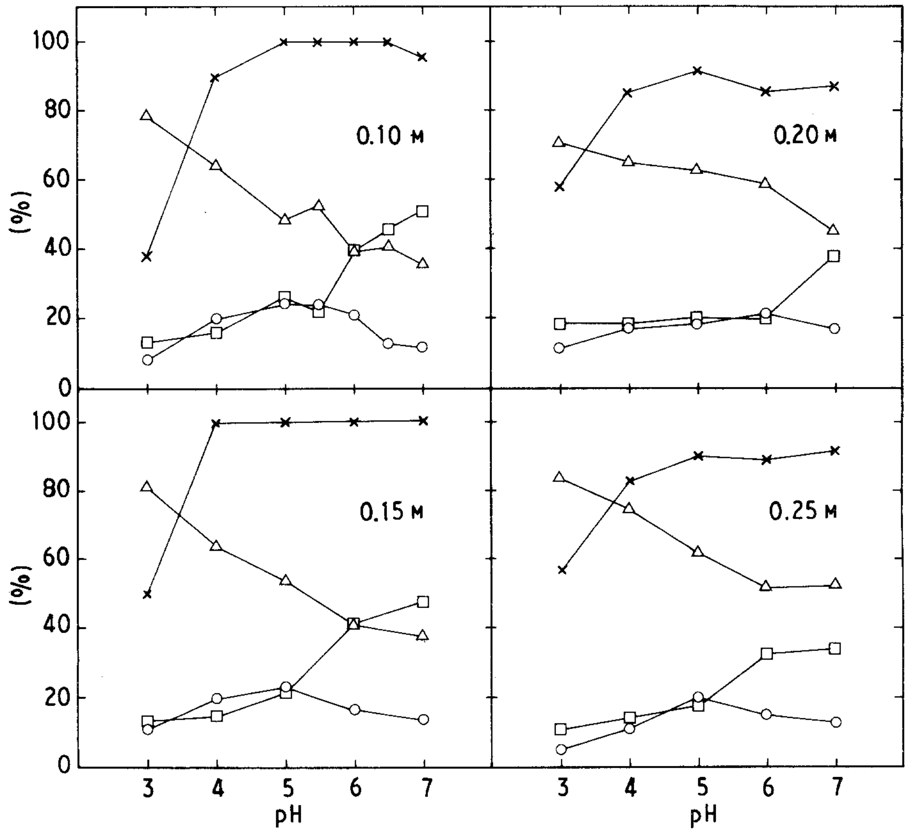

Figure 2 Composition of alloy precipitates as a function of pH for the four concentrations of $NaBH_4$: (○) at % B; (□) at % Ni, (△) at % Fe; (x) percentage of iron in the samples present in the amorphous phase, as estimated using Mössbauer spectroscopy.

the samples prepared at pH values between 3 and 7. The uncertainties are less than about 5 at %. This figure also shows the percentage of iron present in the amorphous alloy phase as estimated from the Mössbauer spectra. At low pH values there is a tendency for the boron content to increase with pH, but for higher pH values the boron content decreases again. The same tendency has been observed in studies of Fe–B particles prepared by similar methods [15]. The nickel content increases with increasing pH whereas the iron content decreases. It is remarkable that for the lowest pH values the Fe:Ni ratio in the precipitates may be larger than 4, which is the ratio in the metal salt solution, but for the highest pH values the Fe:Ni ratio is closer to 1, with some dependence on the $NaBH_4$ concentration. In studies of Fe–Co–B particles it has also been found that the Fe:Co ratio may be larger or smaller than the Fe:Co ratio in the solution, depending on the $NaBH_4$ concentration [10] and pH [16]. The relative amount of amorphous alloy component, seen in the Mössbauer spectra, is of the order of 50 % for all the samples prepared at pH 3. The percentage of this component increases rapidly with increasing pH. For an $NaBH_4$ concentration of 0.10 M all the material is amorphous for pH values between 5 and 6.5. For an $NaBH_4$ concentration of 0.15 M all the material is amorphous for pH values between 4 and 7. For higher $NaBH_4$ concentrations all the samples contain some α-Fe. Thus it is found that only in a limited range of pH values and $NaBH_4$ concentrations are all the iron-containing materials amorphous.

Electron micrographs showed that the samples generally consist of particles with a size ranging from 10–100 nm. Electron diffraction and energy dispersive X-ray spectroscopy (EDS) confirmed the presence of an amorphous phase containing iron and nickel (elements with $Z < 11$ cannot be detected with the type of detector used). Weak diffraction lines indicating the presence of a cubic oxide phase were found showing that the passivation has led to oxidation of a part of the alloys. Mössbauer studies of the passivated samples showed that about 20–25 at % Fe had oxidized to Fe^{3+}.

Fig. 3 shows a micrograph of the sample prepared with 0.10 M $NaBH_4$ at pH 6. The bright-field image shows the size and shape of the amorphous particles and the selected-area diffraction pattern is dominated by two broad lines indicating an amorphous phase. These lines correspond to d-spacings of 0.20 and 0.12 nm (which are typical d-spacings in metallic materials). Two sharp, but weak lines are observed at d-spacings of 0.15 and 0.25 nm corresponding to a small amount of cubic oxide. An EDS analysis showed an Fe:Ni ratio of 1.0 ± 0.1 in agreement with the result of chemical analysis (Fig. 2).

The magnetic hyperfine field of the amorphous phase was estimated by fitting the spectra with Lorentzian lines and the results are shown in Fig. 4. It is seen that for all $NaBH_4$ concentrations there is a minimum at pH $\simeq$ 5. This corresponds to the samples which have the highest boron content. In amorphous $Fe_{1-x}B_x$ ribbons the magnetic hyperfine field at room temperature is nearly independent of the boron content for $0.14 < x < 0.25$, but the presence of nickel leads to a decrease in the hyperfine field with increasing boron content [22]. Therefore, the low hyperfine fields found in the samples with the highest boron concentrations seem to be in accordance with the results obtained in studies of ribbons of amorphous alloys.

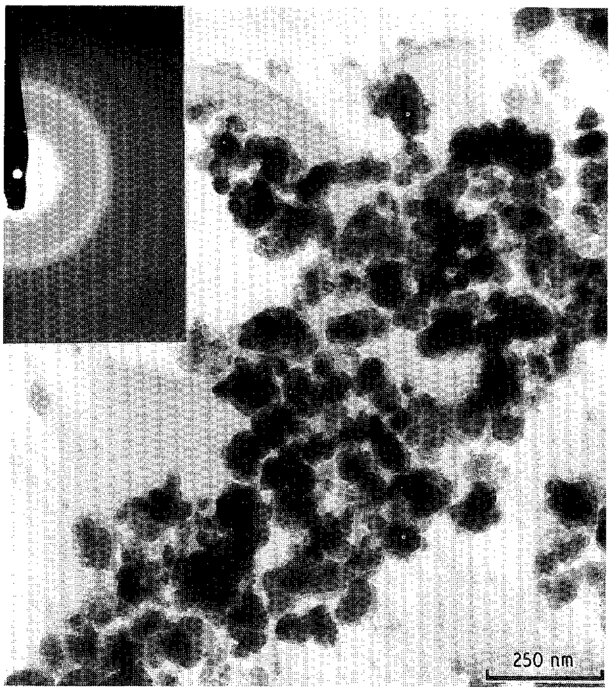

Figure 3 Bright-field electron micrograph and corresponding selected-area electron diffraction pattern of the sample prepared with an $NaBH_4$ concentration of 0.10 M and pH 6.

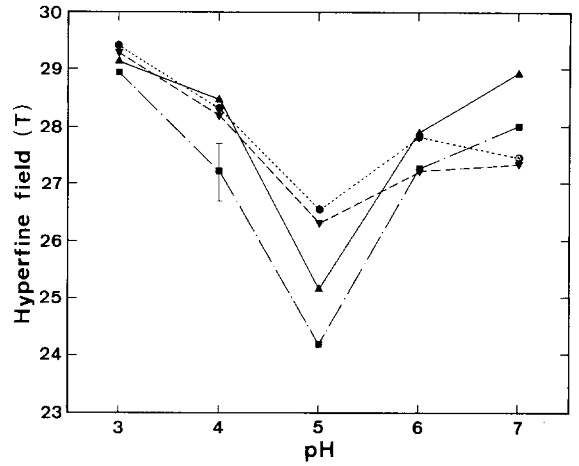

Figure 4 The magnetic hyperfine field of the amorphous phase at 80 K as a function of pH, prepared at various $NaBH_4$ concentrations; (■) 0.10 M; (▲) 0.15 M; (●) 0.20 M; (▼) 0.25 M.

The magnetic hyperfine field of the amorphous components have a maximum value for samples prepared at a pH of 3, but the values are also high for samples prepared at a pH of 7. At these pH values the chemical analysis does not reflect the composition of the amorphous alloy alone, because the samples also contain some α-Fe, but the large magnetic hyperfine fields suggest that the boron contents of the amorphous phases are lower than in the samples containing only amorphous alloy particles.

In several earlier publications, Mössbauer spectra of amorphous Fe–Ni–B ribbons have been reported (see, for example, [22–27]). It is interesting to compare the Mössbauer parameters of the amorphous Fe–Ni–B particles, prepared by chemical reduction, with those of ribbons of similar compositions, but prepared by the liquid-quenching technique. However, only few results of measurements around liquid nitrogen temperature have been reported. Sostarich *et al.* [23] have studied the temperature dependence of the magnetization and the magnetic hyperfine field of amorphous $(Fe_xNi_{1-x})_{80}B_{20}$ ribbons. Two of the present samples contain approximately 20 at % B; the sample prepared with 0.10 M $NaBH_4$, and pH 6 has the composition $Fe_{40}Ni_{40}B_{20}$ and exhibits a magnetic hyperfine field of 27.2 ± 0.5 T at 80 K, and the sample prepared with 0.15 M $NaBH_4$ and pH 4 has the composition $Fe_{65}Ni_{15}B_{20}$ and a magnetic hyperfine field of 28.5 ± 0.5 T. From the results of Sostarich *et al.* [23] we have estimated the magnetic hyperfine fields at 80 K for ribbons with the same compositions to be about 27 and 28 T, respectively. Thus the magnetic hyperfine fields are, within the experimental uncertainties, identical for the ribbons and the particles with the same composition.

4. Conclusions

It has been shown that amorphous Fe–Ni–B particles of various compositions can be prepared by reduction of metal salts in aqueous solution by $NaBH_4$. Only in a limited range of $NaBH_4$ concentrations and pH values of the metal salt solution is a pure amorphous phase formed. The composition of the particles depends on the pH and the $NaBH_4$ concentration. The magnetic hyperfine fields of the amorphous particles, prepared by chemical reduction, are similar to those of amorphous ribbons with similar compositions.

Acknowledgements

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