ANRCP-1999-15
April 1999

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Chemical Synthesis of Magnetic Fe-B and Fe-Co-B Particles and Chains

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Angela L. Woods
Technical Editor

This report was prepared with the support of the U.S. Department of Energy (DOE), Cooperative Agreement No. DE-FC04-95AL85832. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of DOE. This work was conducted through the Amarillo National Resource Center for Plutonium.

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A Report on

Chemical Synthesis of Magnetic Fe-B and Fe-Co-B Particles and Chains

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Submitted for publication to

ANRC Nuclear Program

April 1999

CHEMICAL SYNTHESIS OF MAGNETIC Fe-B AND Fe-Co-B PARTICLES AND CHAINS

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Abstract

With an objective to develop magnetic materials with high saturation magnetization for the Magnetically Assisted Chemical Separation (MACS) process, the chemical synthesis of Fe-B and Fe-Co-B alloys by reducing iron and cobalt chloride solutions with potassium borohydride has been investigated systematically. The influence of the concentration of the reactants, applied magnetic field, reaction atmosphere, and method of mixing the reactants on the microstructure, particle size, composition and magnetic properties has been studied. Both M-B (M = Fe and Co) particles and elongated chains composed of nanometer size M-B particles have been obtained depending on the reaction conditions. The Fe-B samples exhibit saturation magnetization M_s of 120-190 emu/g, remanent magnetization M_r of 10-22 emu/g, and coercive field H_c of 400-900 Oe. A high M_s value of 190 emu/g, which is close to the theoretical value of 218 emu/g for pure Fe, has been achieved particularly for samples with well-defined chain structures. Increasing the Co content in the Fe-Co-B alloys increases the boron content and thereby decreases the crystallinity and M_s values although marginal increase in H_c (1250 Oe) and M_r (36 emu/g) values could be made in some Fe-Co-B compositions. The chain structure with high M_s may be attractive for other magnetic separation processes as well.

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1. INTRODUCTION

There is increasing demand for the development of simple and compact processes for the separation of radioactive and hazardous wastes in DOE sites. Separation techniques such as precipitation and ion exchange are not selective. Solvent extraction is the preferred method, but it is not efficient. In this regard, the Magnetically Assisted Chemical Separation (MACS) process that has been developed at the Argonne National Laboratory is appealing (Buchholz et al, 1997; Kaminski et al, 1997; Nunez et al, 1997). The MACS process is efficient, cost-effective and simple in design.

The MACS process utilizes ferromagnetic microparticles that are coated with selective organic extractants. While the coated extractants separate the radioactive and hazardous species by chemical sorption, the inner magnetic core aids to recover the loaded particles with a magnet. In the MACS process, the extractant-coated magnetic microparticles can be directly mixed in the waste tank or in a mobile reaction vessel and recovered with a magnetic filter. The microparticles loaded with the radioactive and hazardous species can then be vitrified and disposed of as a reduced volume, high-level waste. Alternatively, the contaminated coating can be stripped from the magnetic microparticles so that the particles can be reused.

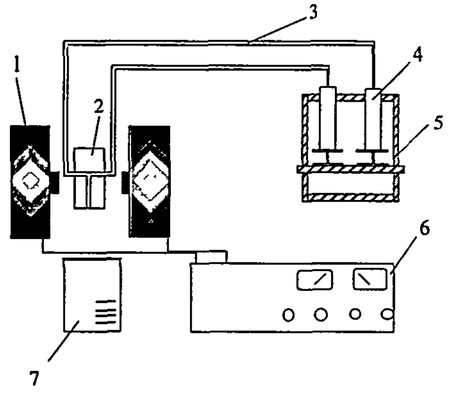
Researchers at the Argonne National Laboratory have utilized for their MACS process a composite consisting of ferrimagnetic Fe_3O_4 (magnetite) particles, charcoal and a cross-linked polyacrylamide (N,N-methylene-bis-acrylamide). This composite is commercially available from Cortex Biochem., Inc. and the Fe_3O_4 particles have sizes in the micrometer range. The efficiency in the separation process may be increased by reducing the size of the magnetic particles. But the reduction in size may result in a decrease in the magnetization per particle, which may cause difficulties in the magnetic recovery of the loaded particles. However, the particle size may be reduced with alternate magnetic materials such as Fe and Fe-Co alloys since they have much higher saturation magnetization per unit volume than Fe_3O_4. In addition, the microstructure of the magnetic particles – spherical particles versus elongated chains – may provide critical advantages in the MACS and other magnetic separation processes.

Our objective is to develop smaller size Fe and Fe-Co alloy particles and chains and evaluate their feasibility for the MACS process. During the past year, we have primarily focused on the chemical synthesis and characterization of Fe and Fe-Co alloys and the results are presented in this report.

2. EXPERIMENTAL PROCEDURE

The Fe and Fe-Co alloys were synthesized by a chemical process involving the reduction of iron chloride or a mixture of iron and cobalt chlorides with potassium borohydride (Schlesinger et al, 1953; van Wonterghem et al, 1986). With an objective to optimize the synthesis and processing procedures, the reduction reactions were carried out with various ratios of metal chloride to borohydride under various conditions. For example, the reactions were carried out (i) in the presence and absence of magnetic field, (ii) in the presence and absence of oxygen (*i. e.* in ambient air and in an argon-filled glove box), (iii) in a laboratory-made T-form reactor, which can mix the metal chloride and borohydride solutions in a controlled manner, and (iv) in a beaker by adding the metal chloride and borohydride solutions slowly to a predetermined volume of water. The schematics of the T-form reactor is shown in Figure 1, which allows the reaction to be carried out in the presence and absence of an applied magnetic field (Zhang and Manthiram, 1996). After the reduction reactions, the solid formed was filtered, washed first with water several times and finally with acetone, and allowed to dry at room temperature. With the variations in the synthesis procedure, a total of about 100 samples were synthesized.

The synthesized samples were characterized by X-ray powder diffraction to identify the phases and degree of crystallinity. Microstructural evaluation was carried out with Transmission Electron Microscopy (TEM). Chemical compositions of the samples were determined by Inductively Coupled Plasma (ICP) analysis. Magnetic measurements were carried out with a SQUID magnetometer. All the samples were annealed in a flowing atmosphere of 90% Ar - 10% H_2 at 400°C before the magnetic measurements to clean any surface oxidation that might have occurred during the synthesis or storage and to improve the crystallinity.



1. Electromagnet
2. T-Form Reactor
3. Tygon Tubing
4. Syringe
5. Syringe Stand
6. DC Power Supply
7. Collecting Beaker

Figure 1: Schematics of the T-form Reactor Employed for the Reduction of Metal Chloride Solutions with Potassium Borohydride to Obtain Fe-B and Fe-Co-B Alloys

3. RESULTS AND DISCUSSION

3.1 Fe-B Particles and Chains

Although the reduction of transition metal ions with alkali metal borohydrides has been investigated by several groups, the reactions have been generally carried out in the absence of applied magnetic field (Schlesinger et al, 1953; van Wonterghem et al, 1987; Saida et al, 1991; Corrias et al, 1993; Glavee et al, 1993). These reactions generally tend to give M-B (M = Fe and Co) particles or net-like structures. On the other hand, a few groups have carried out the reduction reactions in the presence of applied magnetic field (Oppegard et al, 1961; Uehori et al, 1978; Watanabe et al, 1981; Kim and Brock, 1987; Zhang and Manthiram, 1996). The reduction in presence of magnetic field in a T-form reactor (Figure 1) has been shown to give well-organized chain structures under certain conditions (Zhang and Manthiram, 1996).

However, most of these studies pertained to a single, fixed magnetic field and fixed concentrations of metal chloride and borohydride solutions. No systematic investigation of the influence of the magnetic field or concentrations of the reactants on the microstructure and magnetic properties of M-B is available. Also, the reported values of saturation magnetization M_s <160 emu/g (Oppegard et al, 1961; Watanabe et al, 1981; Kim and Brock, 1987; Zhang and Manthiram, 1996) are significantly lower than the theoretical value of 218 emu/g for pure Fe. It may be possible to enhance the M_s values by optimizing the synthesis and processing conditions.

We focused first on the influence of the applied magnetic field during the reduction process. The reduction reactions were carried out in the T-form reactor shown in Figure 1 by mixing equal volumes of 0.1 M $FeCl_2$ and either 0.1 M or 0.5 M KBH_4 solution. The

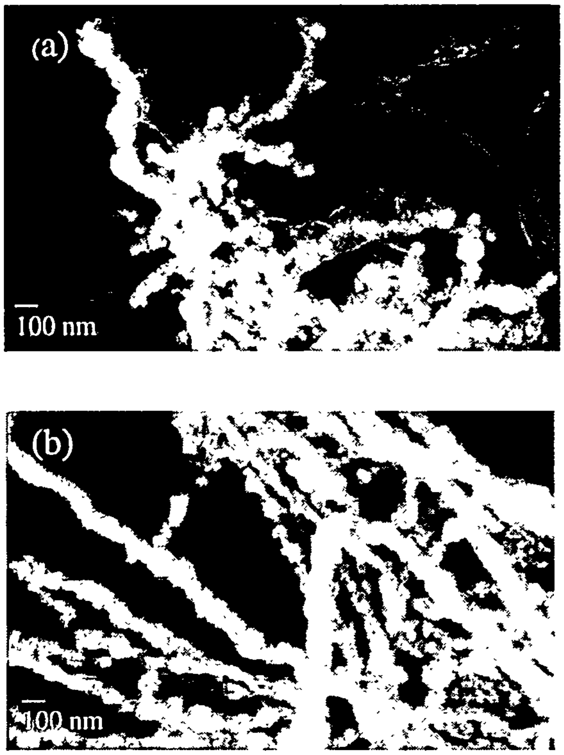


Figure 2: TEM Photographs of the Samples Obtained by Reducing 0.1 M $FeCl_2$ with 0.1 M KBH_4 Solution in the T-form reactor: (a) no magnetic field, and (b) applied magnetic field of 3000 Oe during synthesis.

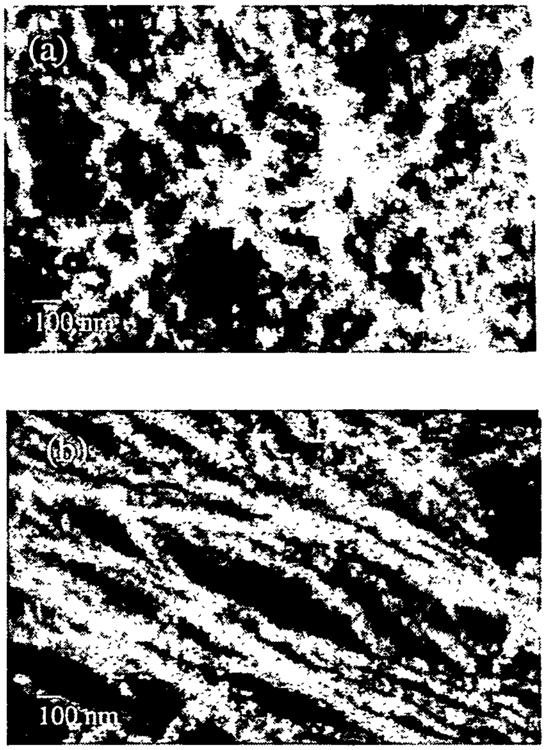


Figure 3: TEM Photographs of the Samples Obtained by Reducing 0.1 M $FeCl_2$ with 0.5 M KBH_4 Solution in the T-form Reactor: (a) no magnetic field, and (b) applied magnetic field of 3000 Oe during synthesis.

TEM photographs of the samples obtained are shown in Figures 2 and 3 for the two concentrations (0.1 and 0.5 M) of KBH_4.

TEM data reveal that while poor chains or net-like structures are formed in the absence of magnetic field (Figures 2a and 3a), a well-defined chain structure is formed in the presence of an applied magnetic field of 3000 Oe (Figures 2b and 3b). The tendency to form the chain structure was found to increase with increasing magnetic field and the chain structure becomes increasingly straight with increasing applied field during the synthesis.

With 0.1 M KBH_4 solution, the particle size was found to decrease from about 50 to 25 nm as the magnetic field increases from 0 to 2000 Oe, and then to increase to 75 nm as the field increases to 3000 Oe. On the other hand, with a higher concentration (0.5 M) of KBH_4, the particle size was found to remain nearly constant around 50-60 nm for the entire magnetic field range of 0 – 3000 Oe.

The X-ray diffraction patterns of the samples are shown in Figures 4 and 5, respectively, for the 0.1 and 0.5 M of KBH_4 solutions. The observed diffraction peaks correspond to BCC iron. The crystallinity of the as-prepared samples seems to be enhanced with increasing magnetic field. Also, the crystallinity of the samples becomes enhanced on annealing at 400°C as indicated by the sharper diffraction peaks.

The variations of boron content with the applied magnetic field are shown in Figures 6a and 7a for the two concentrations (0.1 and 0.5 M) of KBH_4. With both 0.1 and 0.5 M KBH_4, the boron content does not vary significantly with the synthesis field. The boron contents remain nearly constant around 14 ± 3 atom% and the samples synthesized at 3000 Oe having the highest boron contents.

The variations of saturation magnetization M_s, coercive field H_c, and remanent magnetization M_r with the applied magnetic field used during synthesis are also shown in Figures 6 and 7 for the two concentrations (0.1 and 0.5 M) of KBH_4. Figure 8 shows the hysterisis loop for a few representative samples. With both 0.1 and 0.5 M KBH_4, the M_s values increase with increasing synthesis field (Figures 6b and 7b) and reach a maximum of about 190 emu/g, which is slightly lower than the theoretical value of 218 emu/g for pure Fe. The slightly lower M_s value compared to the theoretical value could be due to the presence of significant amount of boron in the samples. The data reveal that the well-defined and straight chain structures give the highest M_s values. More importantly, our highest M_s values (190 emu/g) are much higher than the highest M_s values (< 160 emu/g) reported in the literature (Oppegard et al, 1961; Watanabe et al, 1981; Kim and Brock, 1987; Saida et al, 1991; Zhang and Manthiram, 1996) for samples prepared in presence of an applied magnetic field. The higher M_s values of our samples could be due to the straight chain structure with controlled particle size and composition and due to the cleaning of the oxidized surfaces and enhancement in crystallinity on annealing. The latter conclusion is supported by the fact that the as-prepared samples generally showed lower M_s values than the annealed samples.

The M_r values are much lower than the M_s values (Figures 6c and 7c). The M_r values decrease from 18 to 10 emu/g with increasing synthesis field for 0.1 M KBH_4. On the other hand, the M_r value tends to decrease initially from 21 to 16 emu/g as the synthesis field increases from 0 to 1500 Oe, and then increases to 22 emu/g at 3000 Oe for 0.5 M KBH_4. The H_c values decrease from 625 to 425 Oe with increasing synthesis field for 0.1 M KBH_4 (Figure 6d). On the other hand, the H_c value tends to decrease initially from 700 to 600 Oe as the synthesis field increases from 0 to 1500 Oe, and then increases to 900 Oe at 3000 Oe for 0.5 M KBH_4 (Figure 7d). The variations in M_r and H_c values with synthesis field follow similar trends.

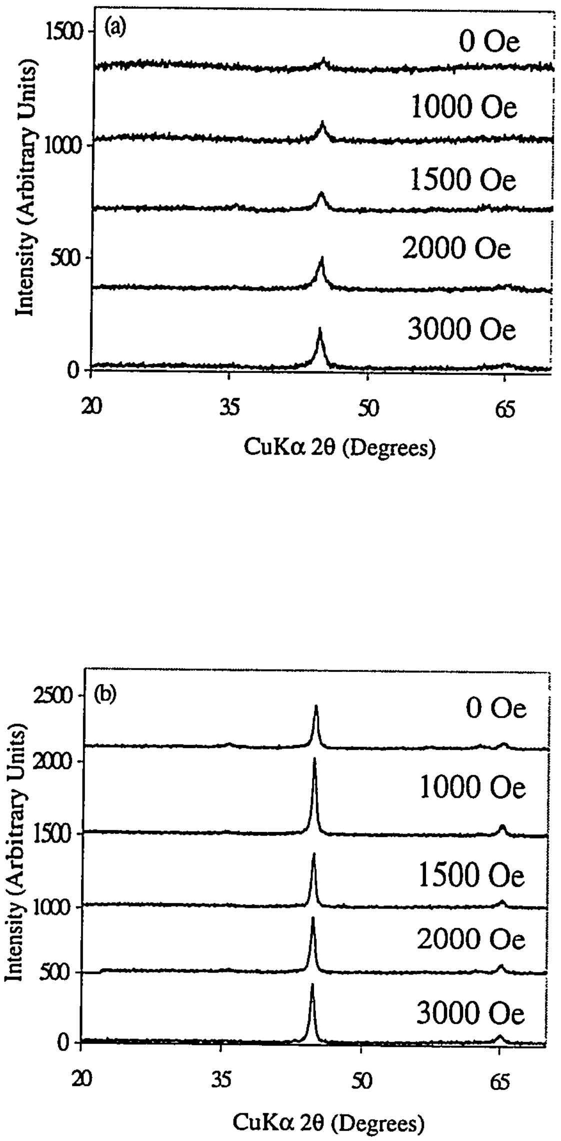


Figure 4: X-Ray Diffraction Patterns of the Samples Prepared by Reducing 0.1 M $FeCl_2$ with 0.1 M KBH_4 at Various Magnetic Field: (a) as-prepared samples, and (b) after annealing at 400°C for 1 h in 90% Ar – 10% H_2 atmosphere.

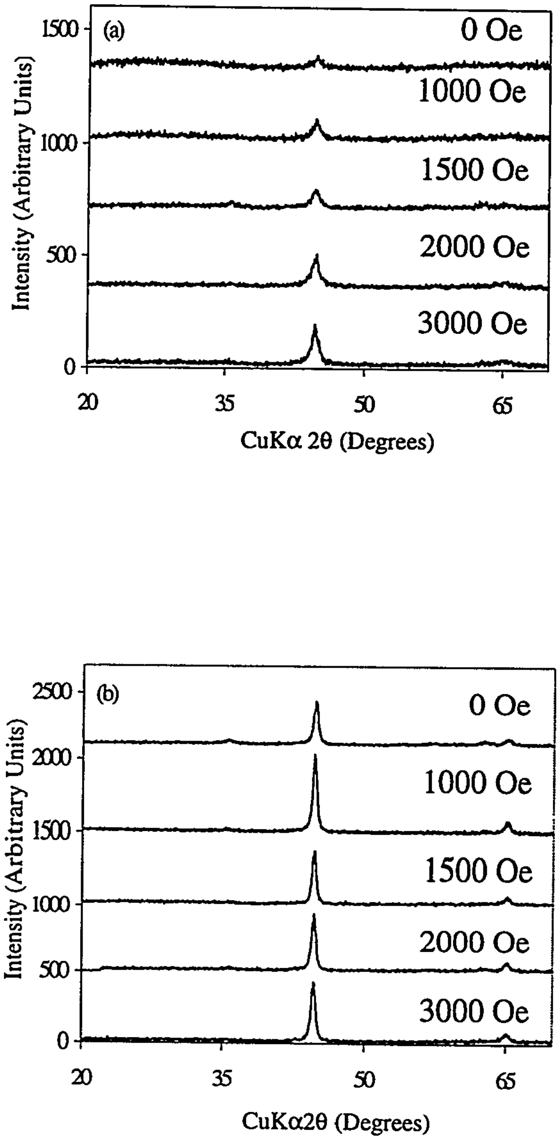


Figure 5: X-Ray Diffraction Patterns of the Samples Prepared by Reducing 0.1 M $FeCl_2$ with 0.5 M KBH_4 at Various Magnetic Field: (a) as-prepared samples, and (b) after annealing at 400°C for 1 h in 90% Ar – 10% H_2 atmosphere.

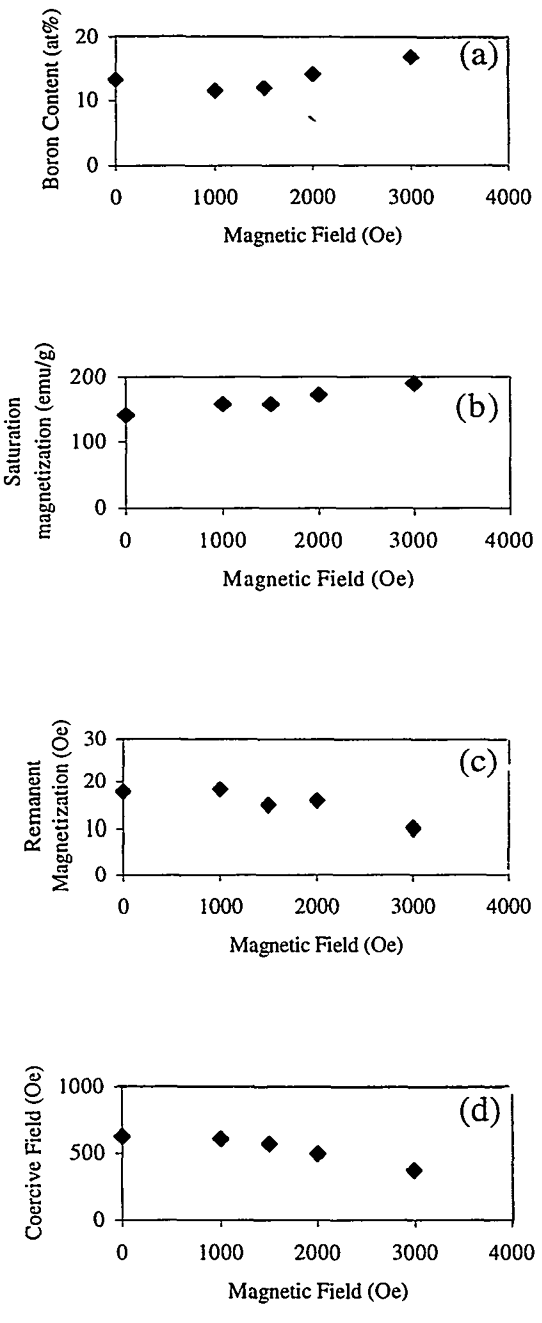


Figure 6: Variations of (a) Boron Content, (b) Saturation Magnetization M_s, (c) Remanent Magnetization M_r, and (d) Coercive Field H_c with the Applied Magnetic Field Used During Synthesis. The reduction was carried out with 0.1 M $FeCl_2$ and 0.1 M KBH_4 solutions.

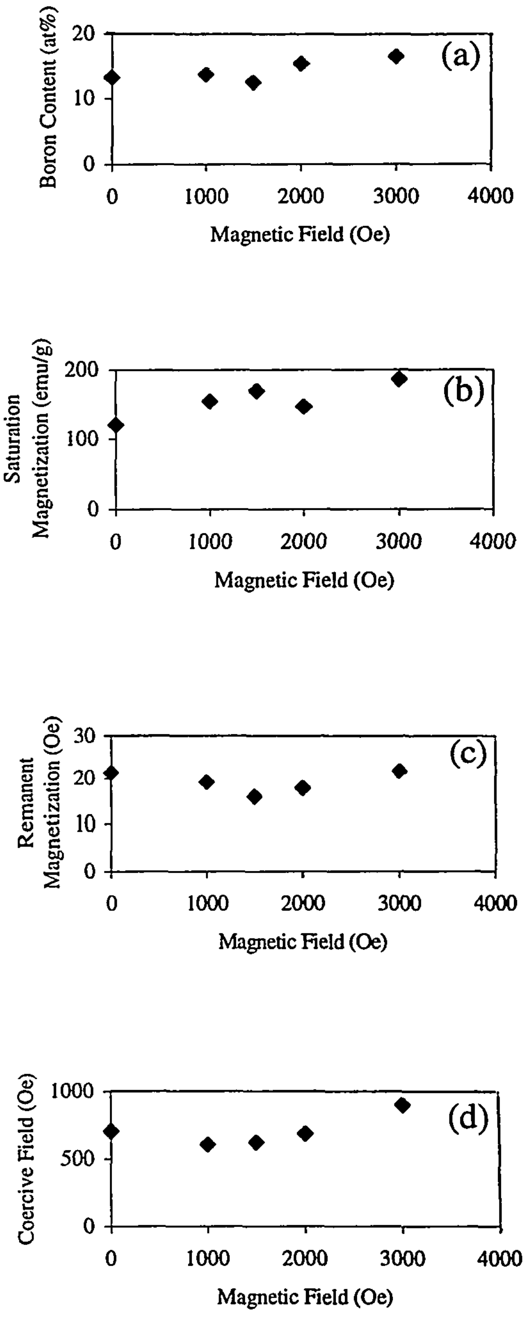


Figure 7: Variations of (a) Boron Content, (b) Saturation Magnetization M_s, (c) Remanent Magnetization M_r, and (d) Coercive Field H_c with the Applied Magnetic Field Used During Synthesis. The reduction was carried out with 0.1 M $FeCl_2$ and 0.5 M KBH_4 solutions.

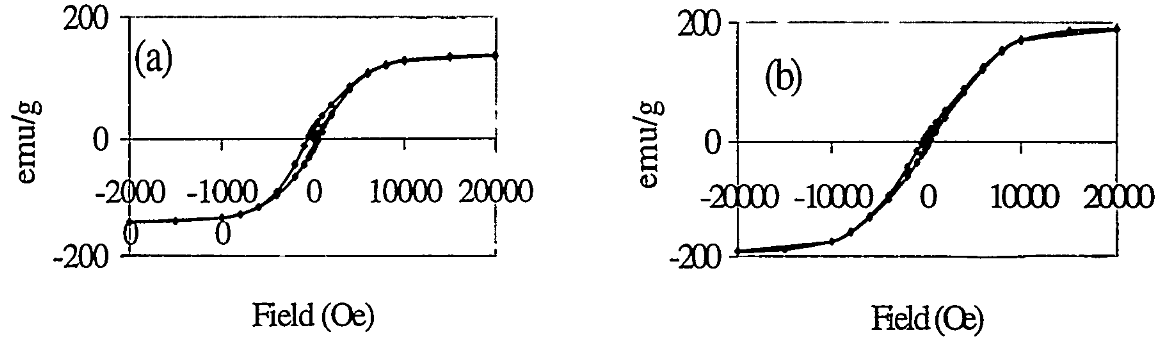


Figure 8: Hysterisis Loops of the Fe-B Samples Synthesized by Reducing 0.1 M $FeCl_2$ with 0.1 M KBH_4 in the T-form reactor: (a) no magnetic field, and (b) applied magnetic field of 3000 Oe during synthesis.

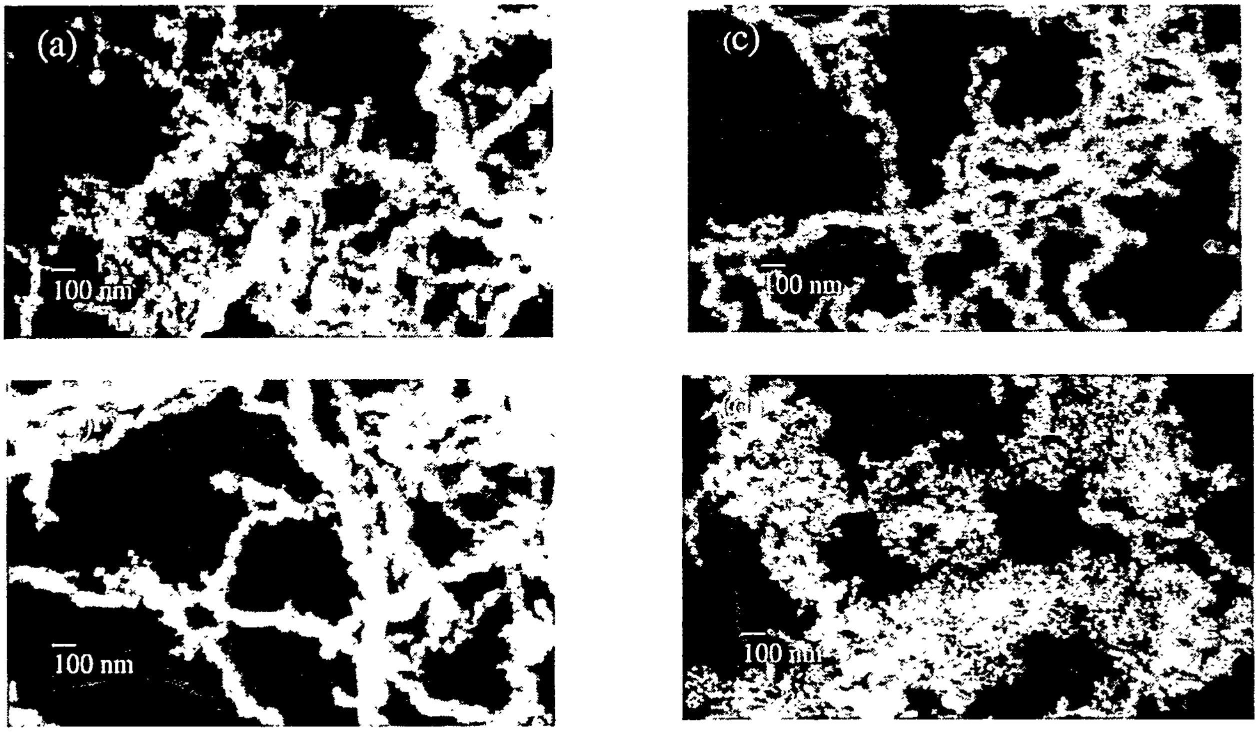


Figure 9: TEM Photographs of the Samples Obtained with the Reduction of 0.1 M $FeCl_2$ and Various Concentrations of KBH_4 in the Absence of a Magnetic Field in the T-form Reactor: (a) 0.05 M KBH_4, (b) 0.1 M KBH_4, (c) 0.5 M KBH_4, and (d) 2 M KBH_4.

In order to understand further the influence of the concentration of KBH_4, we have also carried out synthesis experiments in the T-form reactor with varying concentrations of KBH_4 both in the absence of magnetic field and at a constant applied field of 1500.

Figure 9 shows the TEM photographs of the samples prepared with various concentrations of borohydride in the absence of magnetic field. The microstructure changes from a net-like or poor chain structure to particle-like structure as the borohydride concentration increases. The particle size tends to decrease with increasing concentration of borohydride (Figure 10a). The sample prepared with a very low concentration (0.05 M) of borohydride has a range of particle size from 25-100 nm. The X-ray diffraction patterns recorded before and after annealing appear similar to those given in Figures 4 and 5. The crystallinity does not change much with the concentration of borohydride. The boron content decreases initially from 18 to 13 atom % as the borohydride concentration increases from 0.05 to 0.5 M and then increases to 21 atom % for 1-2 M KBH_4 (Figure 10b). The variations of M_s, M_r, and H_c with KBH_4 concentration are also shown in Figure 10. While the M_s values decrease, the H_c and M_r values increase as the borohydride concentration increases from 0.1 to 2 M. The increase in H_c and M_r with decreasing particle size is due to a transition from multi-domain to single-domain particles (Kronmuller, 1991; Zhang and Manthiram, 1996). It has been shown previously that the size range of 28-35 nm

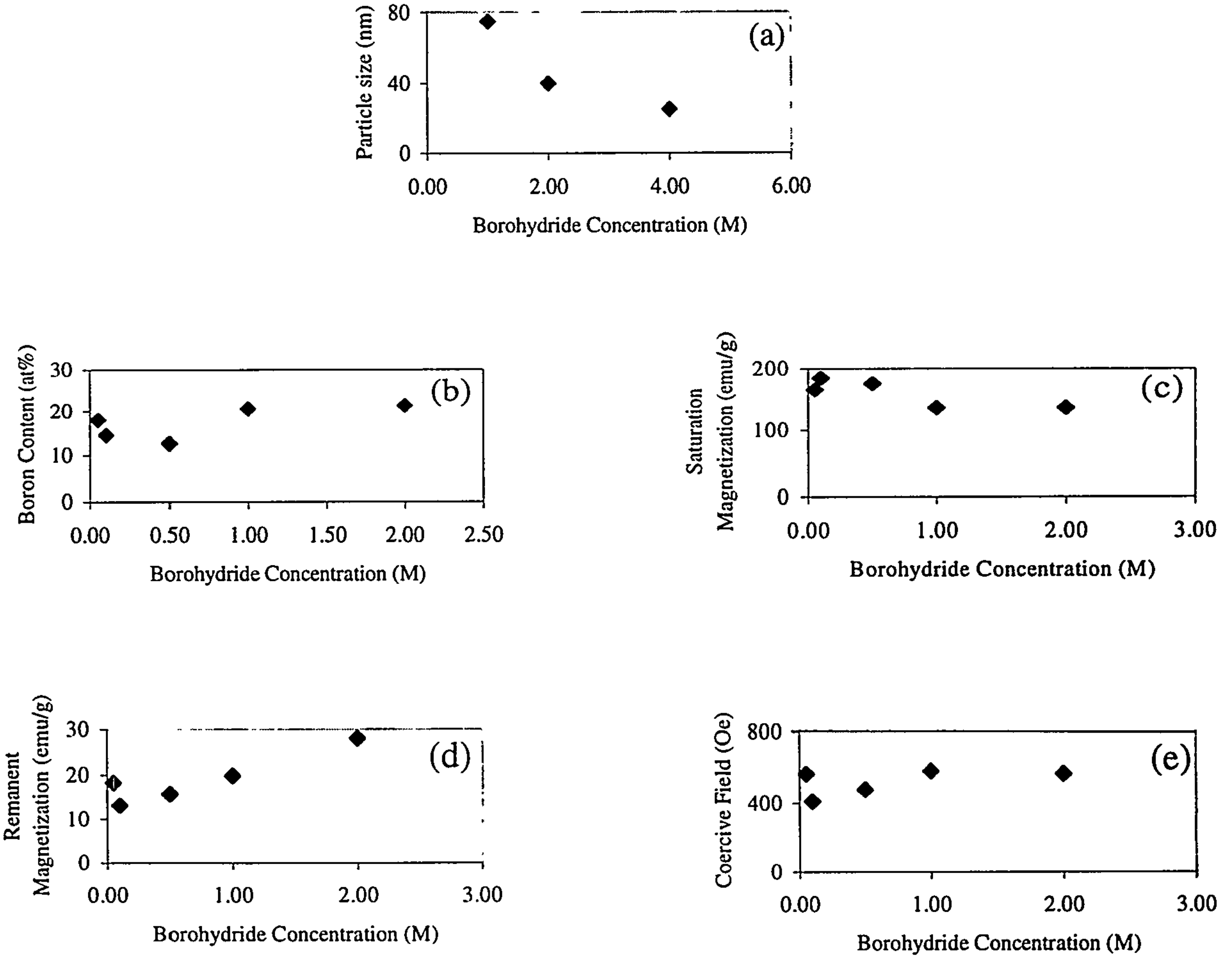


Figure 10: Variations of (a) Particle Size, (b) Boron Content, (c) Saturation Magnetization M_s, (d) Remanent Magnetization M_r, and (e) Coercive Field H_c with KBH_4 Concentration. The reduction was carried out in the T-form reactor with 0.1 M $FeCl_2$ and various concentrations of KBH_4 in the absence of magnetic field.

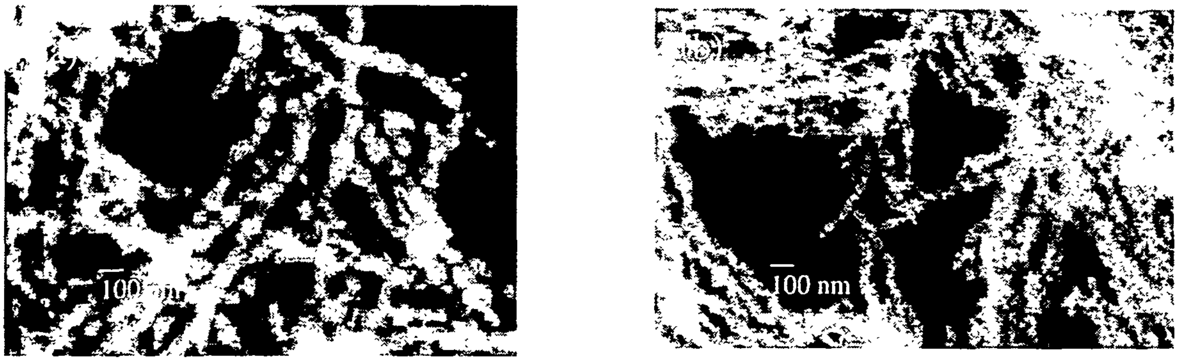


Figure 11: TEM Photographs of the Samples Obtained in the T-form Reactor by the Reduction of 0.1 M $FeCl_2$ with Various Concentrations of KBH_4 in the Presence of a Magnetic field of 1500 Oe: (a) 0.05 M KBH_4, and (b) 2 M KBH_4.

corresponds to single-domain region (Zhang and Manthiram, 1996). However, this size range may be influenced slightly by the boron content. Also, the decrease in M_s values at higher borohydride concentrations could be due to the possibility of a small fraction of superparamagnetic particles at smaller particle size (Zhang and Manthiram, 1996).

Figure 11 shows the TEM photographs of the samples prepared with various concentrations of borohydride at a constant magnetic field of 1500 Oe. All the samples show chain structure due to the presence of magnetic field during synthesis. The particle size tends to decrease with increasing concentration of borohydride (Figure 12a) as in Figure 10a. The X-ray diffraction patterns recorded before and annealing appear similar to those given in Figures 4 and 5 and the crystallinity does not change much with the concentration of borohydride. The boron content increases from 12 to 22 atom% as the borohydride concentration increases from 0.05 to 2 M (Figure 12b). The variations of M_s, M_r, and H_c with KBH_4 concentration are also shown in Figure 12. The M_s values remain nearly constant around 160 emu/g up to a borohydride concentration of 0.5 M, and then decreases to 140 emu/g as the borohydride concentration increases to 1-2 M (Figure 12c). The M_r and H_c values remain nearly constant around 16 emu/g and 600 Oe, respectively, up to a borohydride concentration of 0.5 M, and increases thereafter to approximately 20 emu/g and 700-800 Oe as the borohydride concentration increases to 1-2 M (Fig. 12d and 12e). As discussed in the previous paragraph, the increase in H_c and M_r values at higher borohydride concentrations could be due to a transition from multi-domain to single-domain particles as the particle size decreases. Similarly the decrease in M_s values at smaller particle size could be due to the presence of superparamagnetic particles.

In order to understand the influence of the method of mixing the reactants, we also carried out experiments by adding equal volumes of 0.1 M $FeCl_2$ and various concentrations of KBH_4 from two syringes into a beaker containing 20 ml of water in the absence of magnetic field. Figure 13 shows the TEM photographs of the samples prepared with various concentrations of KBH_4. All the samples show a net-like structure. It is interesting to note that the samples prepared by this method with 2 M borohydride shows a net-like structure (Figure 13b) while the sample prepared in the T-form reactor at the same concentration of borohydride shows a particle structure (Figure 9d). These samples had a wide range of particle size from 25 to 100 nm. The X-ray diffraction patterns recorded before and annealing appear similar to those given in Figures 4 and 5 and the crystallinity does not change much with the concentration of borohydride. The boron

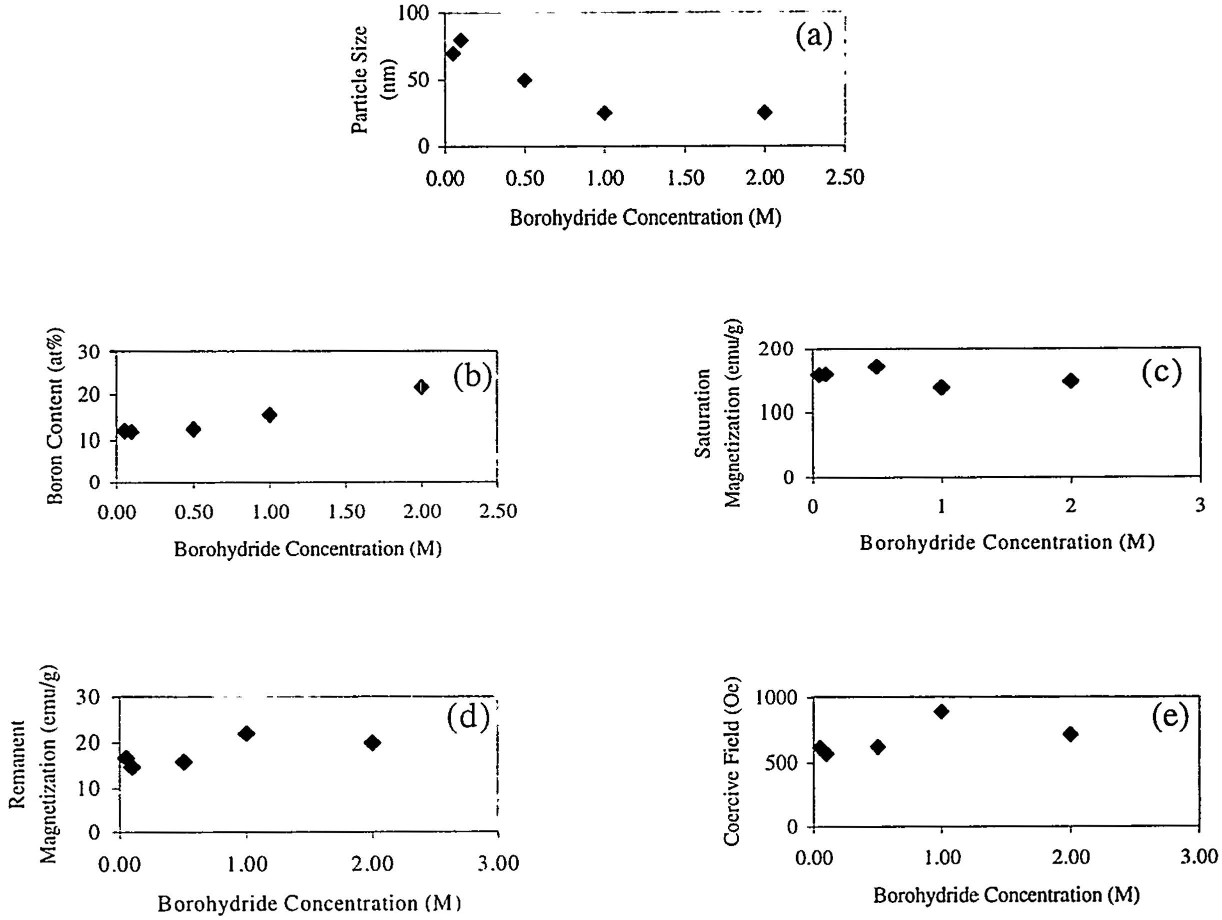


Figure 12: Variations of (a) Particle Size, (b) Boron Content, (c) Saturation Magnetization M_s, (d) Remanent Magnetization M_r, and (e) Coercive Field H_c with KBH_4 Concentration. The reduction was carried out in the T-form reactor in the presence of a magnetic field of 1500 Oe with 0.1 M $FeCl_2$ and various concentrations of KBH_4.

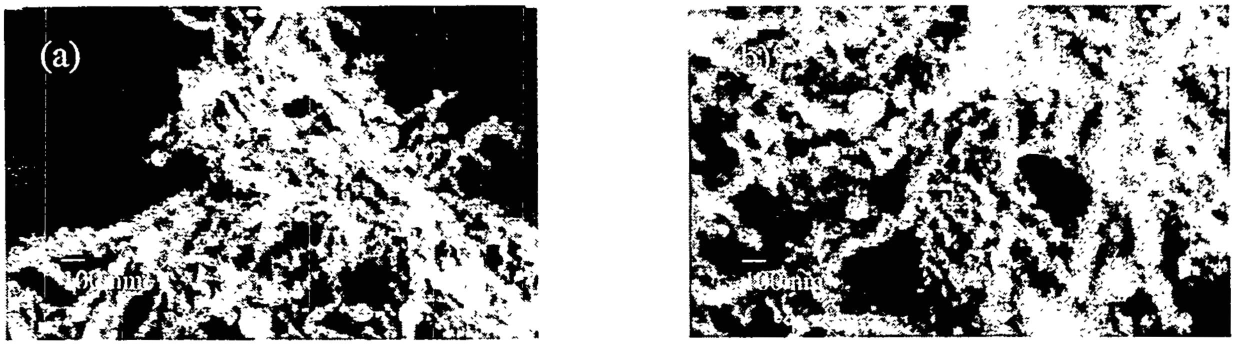


Figure 13: TEM Photographs of the Samples Obtained by the Reduction of 0.1 M $FeCl_2$ with Various Concentrations of KBH_4: (a) 0.05 M KBH_4, and (b) 2 M KBH_4. The reduction was carried out by adding equal volumes of $FeCl_2$ and KBH_4 from two syringes into a beaker containing 20 ml of water in the absence of magnetic field.

content decreases from 22 to 15 atom % as the borohydride concentration increases from 0.05 to 0.5 M and then remains almost constant for 0.5-2 M (Figure 14a). The variations of M_s, M_r, and H_c with KBH_4 concentration are also shown in Figure 14. The M_s values remain high around 170-180 emu/g for borohydride concentrations of 0.05-1 M, and then decrease to 150 emu/g for 2 M borohydride (Figure 14b). The M_r values increase from 12 to 20 emu/g as the borohydride concentration increases from 0.05 to 1 M and then decreases to 17 emu/g for 2 M KBH_4. Similarly, the H_c values increase from 450 to 650 Oe as the borohydride concentration increases from 0.05 to 1 M and then decreases to 570 Oe for 2 M KBH_4. The wide range of particle size makes the correlation of magnetic properties to particle size difficult in this case.

In order to understand the influence of the reaction atmosphere, we also carried out experiments in an argon-filled glove box by adding equal volumes of $FeCl_2$ and KBH_4 from two syringes into a beaker containing 20 ml of water in the absence of magnetic field. These samples were found to contain much higher boron contents (20-40 atom%) compared to the other samples discussed earlier. As a result, the as-prepared samples were generally found to be amorphous compared to the other samples. TEM data show either net-like structure or particle structure. The high boron content leads to a

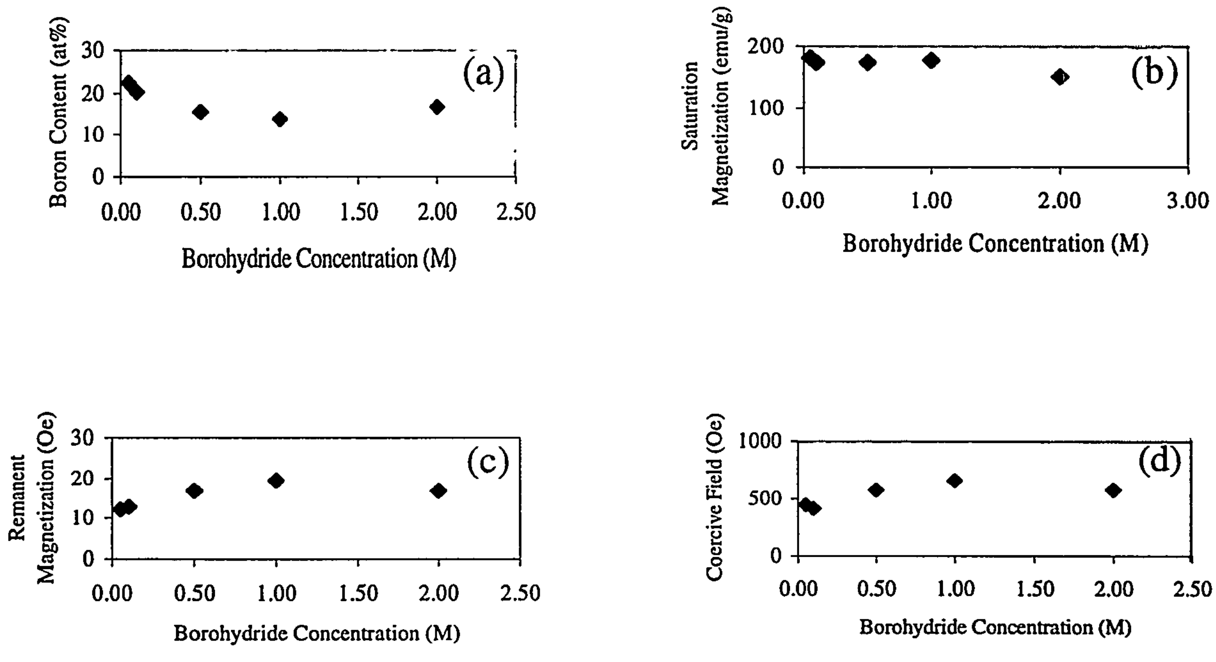


Figure 14: Variations of (a) Boron Content, (b) Saturation Magnetization M_s (c) Remanent Magnetization M_r, and (d) Coercive Field H_c with KBH_4 Concentration. The reduction was carried out by adding equal volumes of $FeCl_2$ and KBH_4 from two syringes into a beaker containing 20 ml of water in the absence of magnetic field.

much lower M_s values for these samples, which are not attractive for our objective.

3.2 Fe-Co-B Particles and Chain

In the Fe-Co system, the M_s value is known to increase with increasing Cobalt content, reach a maximum around 35 atom % Co, and then decrease. Therefore, with an objective to obtain alloys with highest possible M_s value, we investigated the synthesis of Fe-Co-B compositions.

First, we explored the reduction of 0.1 M solutions of a mixture consisting of iron and cobalt chlorides with 0.1 M KBH_4 in the T-form reactor at an applied magnetic field of 1500 Oe for various Co contents. The TEM photographs of the samples obtained with various Co contents are shown in Figure 15. The data show that the chain structure is maintained up to about 30 atom % Co. For Co contents > 50 atom %, particles are formed without any chain structure. As the Co content increases, the particle size decreases and boron content increases (Figure 16). The increase in boron content and decrease in particle size cause a decrease in crystallinity with increasing Co content as indicated by X-ray diffraction.

Figure 16 also shows the variations of M_s, M_r, and H_c with Co content. The M_s value remains nearly constant around 165 emu/g up to a Co content of 30 atom % and then decreases with increasing Co content. The M_r and H_c values increase with Co content up to about 50 atom % Co and then decrease. The incorporation of Co does not help to increase the M_s value, which is in contrast to that expected for the Fe-Co alloys. However, the incorporation of Co helps to increase the M_r and H_c values significantly up to about a Co content of 50 atom %. The decrease in M_s values at higher Co contents is due to the increase in B content and the decrease in crystallinity. Similarly the drastic decrease in H_c and M_r for Co contents > 50 atom % is due to the decrease in crystalline anisotropy caused by the increasing boron content.

We also investigated the synthesis of the

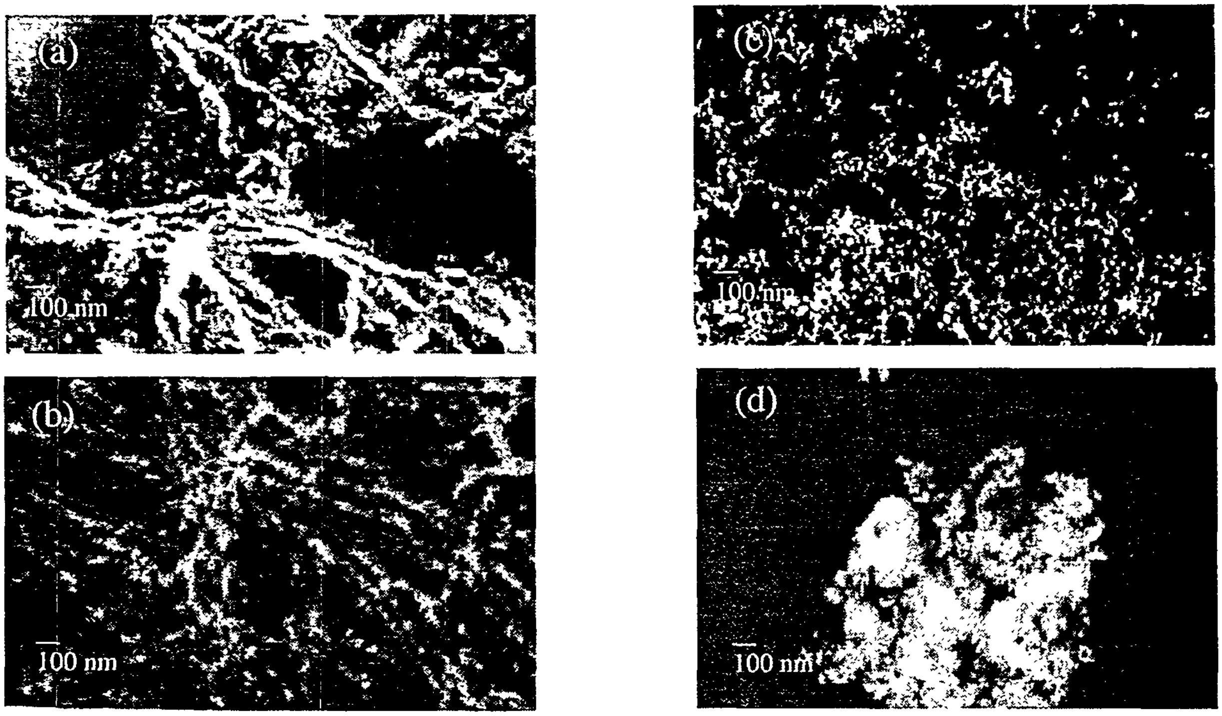


Figure 15: TEM Photographs of the Samples Obtained in the T-form Reactor by the Reduction of 0.1 M Solutions Consisting of a Mixture of $FeCl_2$ and $CoCl_2$ with 0.1 M KBH_4 in the Presence of a Magnetic Field of 1500 Oe. (a) 0 atom % Co, (b) 30 atom % Co, (c) 50 atom % Co, and (d) 100 atom % Co.

composition 70 atom % Fe– 30 atom % Co, which is expected to have the highest M_s value, under various conditions. For example, it was pursued by varying the magnetic field in the T-form reactor, varying the concentrations of the borohydride, varying the reaction atmosphere from air to argon, and adding the reactants from two syringes into 20 ml of water in a beaker. All the samples obtained by these procedures show a M_s value < 170 emu/g, and are thus inferior to the Fe-B samples. However, the H_c values could be increased significantly to as high as 1200 Oe in some compositions.

4. CONCLUSIONS

With an objective to maximize the saturation magnetization values, the chemical synthesis of Fe-B and Fe-Co-B alloys have been investigated systematically by reducing the metal chloride solutions with potassium borohydride under various conditions. Various combinations of M_s and H_c values and microstructures – straight chains, net-like structures, and particles – could be achieved depending on the reaction conditions. The systematic investigation has helped to identify optimum reaction conditions that give much higher M_s values (190 emu/g) than those (160 emu/g) reported in the literature.

The next task is to coat the Fe-B alloys with a cross-linked polymer and the organic extractant to make them suitable for the Magnetically Assisted Chemical Separation (MACS) Process. Agglomeration of the Fe-B chains and particles will be an important obstacle in this task. To overcome this difficulty, we are currently exploring the use of surfactants during the synthesis process. Preliminary results show that well dispersed Fe-B magnetic chains without much agglomeration can be obtained employing suitable surfactants. Coating of the Fe-B alloys with the polymer is currently in progress.

In addition to the MACS process, the unique microstructures – such as the straight chain structures – obtained by this chemical synthesis procedure combined with a high saturation magnetization may make these alloys attractive for other magnetic separations as well.

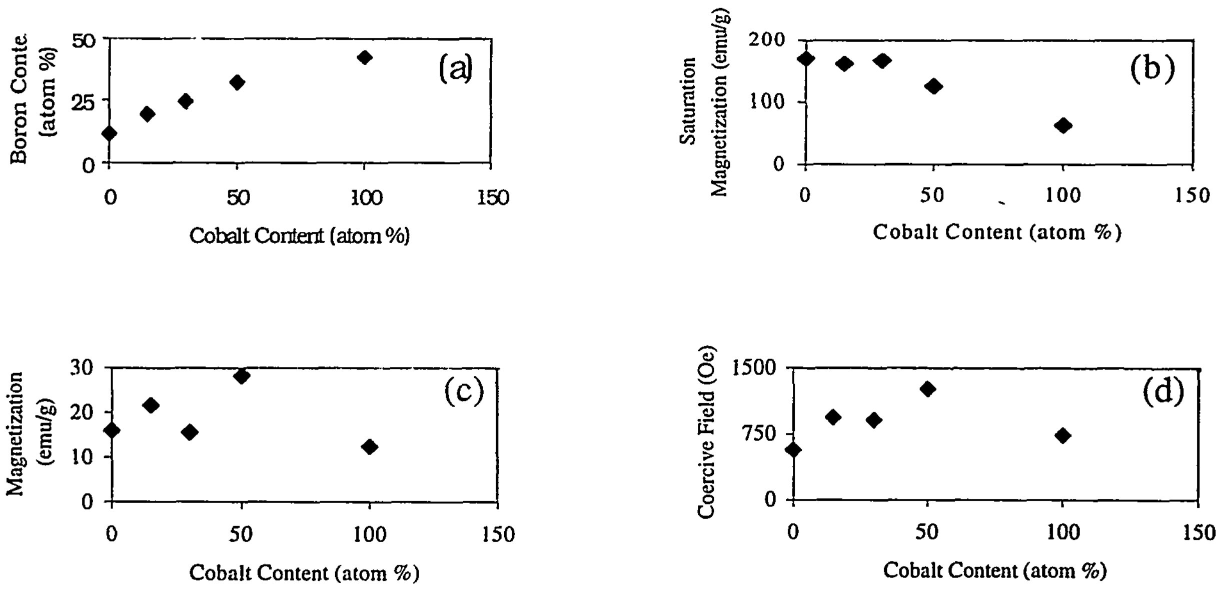


Figure 16: Variations of (a) Boron Content, (b) Saturation Magnetization M_s, (c) Remanent Magnetization M_r, and (d) Coercive Field H_c with Cobalt Content. The samples were obtained in the T-form reactor by the reduction of 0.1 M solutions consisting of a mixture of $FeCl_2$ and $CoCl_2$ with 0.1 M KBH_4 in the presence of an applied magnetic field of 1500 Oe.

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