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Chemically prepared Fe–B ultrafine amorphous alloy particles: influence of the way of mixing reactants

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Fe–B ultrafine amorphous alloy particles have been prepared by the addition of $FeSO_4$ solutions into KBH_4 solutions. The reaction was found to automatically maintain constant pH levels in a basic medium and produced Fe–B samples with higher boron content as compared to the reaction for the addition of KBH_4 solutions into $FeSO_4$ solutions. The latter reaction automatically maintained constant pH levels in an acidic medium. The mechanism of the overall reaction between $FeSO_4$ and KBH_4 in aqueous solution is composed of three simple independent reactions which are shown to be valid for both addition routes for the reaction. The concentration and addition rate of $FeSO_4$ solutions were also found to significantly influence the boron content and properties of the produced Fe–B samples.

1. Introduction

Chemical reduction is a useful way to prepare ultrafine amorphous alloy particles (UFAAP), which may be used as magnetic materials and catalysts [1–10]. The preparation and properties of the UFAAP have been extensively investigated [2, 3, 11–15]. In our previous papers, we have studied the mechanism of the reactions which occurred by adding solutions of potassium borohydride into solutions of iron cations [15, 16]. We have suggested that the overall reaction between Fe^{2+} and borohydride in aqueous solution consist of three simple independent reactions [15]. The mechanism was successful in predicting the boron content in the Fe–B UFAAP products prepared when the solutions of potassium borohydride were added into the solutions of iron cations [15, 16]. However, from pH versus time curves for the reaction, we found that the reaction proceeded in different ways when mixing the reactants differently. This may be the reason why the ways of mixing the reactants greatly influence the properties of the produced Fe–B UFAAP [13, 17]. In this respect, the mechanism should be re-discussed for the reaction when Fe^{2+} solutions are added into solutions of borohydride. In addition, some important conclusions based on this study and references [3, 14, 15] are summarized in this paper concerning the effects of preparation parameters.

2. Experimental procedure

The reaction for the preparation of Fe–B UFAAP in this work was carried out by adding $FeSO_4$ solutions into KBH_4 solutions. Specifically, $FeSO_4$ solutions with different concentrations were added at different rates into a 200 ml KBH_4 solution containing about 0.06 mol KBH_4. The apparatus used has been described elsewhere [15]. Solutions of potassium borohydride were freshly prepared as needed and their pH were adjusted to about 12 to prevent hydrolysis before the reaction. The reaction temperature was controlled at 293 K. The pH value and volume of hydrogen evolved throughout the reaction were monitored by an Orion EA-920 ion analyser and a wet-test meter, respectively. After reactions, the black precipitates were filtered, washed first with distilled water to remove the reaction residues and then with acetone to remove water. The samples were then passivated in nitrogen containing ~1% oxygen, followed by characterization with inductively coupled plasma spectroscopy (ICP), ^{57}Fe Mössbauer spectroscopy, transmission electron microscopy (TEM) and differential scanning calorimetry (DSC).

3. Results and discussion

Fig. 1 shows the pH versus time curves for the reaction between Fe^{2+} and BH_4^- in aqueous solution with different addition directions. It is seen that the two reaction processes are quite different. The reaction proceeded in acidic or basic mediums when adding BH_4^- into Fe^{2+} or *vice versa*. In a previous paper [15], we proposed three independent reactions which are composed of electrode half-reactions based on the assumption that the reducing agent BH_4^- gives out $4e^-$ during the reaction in an acidic medium. In this paper, we first discuss the half-reactions in a basic medium. When an $FeSO_4$ solution was added into a basic KBH_4 solution, the half-reactions for

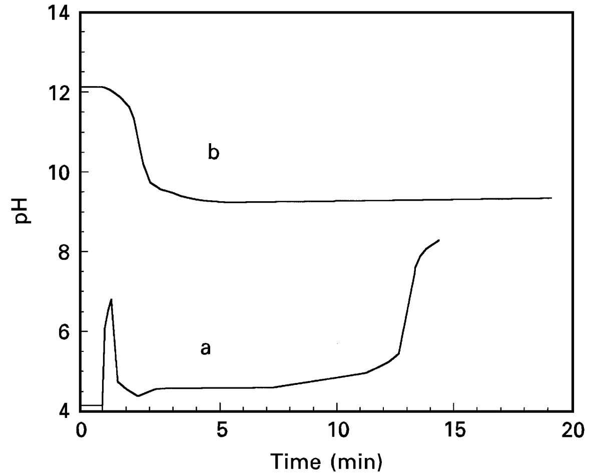

Figure 1 Typical reaction processes for the preparation of Fe–B UFAAP indicated by the change of pH versus time: (a) addition of KBH_4 solution into $FeSO_4$ solution and (b) addition of $FeSO_4$ solution into KBH_4 solution.

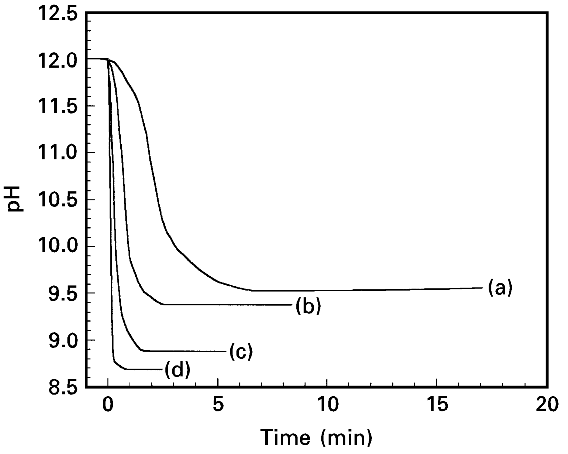

Figure 2 pH versus time curves for the reactions when $FeSO_4$ solutions with initial concentrations of: (a) 3.94×10^{-5} mol per l, (b) 1.7×10^{-4} mol per l, (c) 2.94×10^{-4} mol per l and (d) 3.71×10^{-4} mol per l were added into the KBH_4 solutions.

reductions are:

$$Fe^{2+} + 2e^- = Fe \qquad \phi^0 = -0.44\ V \tag{1}$$

$$2H_2O + 2e^- = H_2\uparrow + 2OH^- \qquad \phi^0 = -0.83 \tag{2}$$

It has been reported in the literature [18] that the reducing agent BH_4^- gives out $8e^-$ in a basic medium:

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e^- \qquad \Delta G^0 = -966.50\ kJ\ mol^{-1} \tag{3}$$

The standard electrode potential, ϕ^0, of this half-reaction is calculated to be -1.25 V, which is higher than -1.67 V for the following half-reaction in which BH_4^- gives out $4e^-$:

$$BH_4^- + 4OH^- = BO_2^- + 2H_2O + 2H_2\uparrow + 4e^- \qquad \phi^0 = -1.67\ V \tag{4}$$

Apparently, BH_4^- is a stronger reducing agent to release $4e^-$ than $8e^-$ even in a basic medium. Combination of the electrode half-reactions shown in Equations 2 and 4 gives the reaction:

$$BH_4^- + 2H_2O = BO_2^- + 4H_2\uparrow \tag{5}$$

And the reduction of iron can be expressed as:

$$BH_4^- + 2Fe^{2+} + 4OH^- = 2Fe + BO_2^- + 2H_2O + 2H_2\uparrow \tag{6}$$

when BH_4^- gives out $4e^-$. The formation of boron still follows the equation [15]:

$$BH_4^- + H_2O = B + OH^- + 2.5H_2\uparrow \tag{7}$$

These independent equations are exactly the same as those for the reaction when solutions of BH_4^- were added into solutions of Fe^{2+} [15]. Now, we determine the validity of these independent equations for the reaction when solutions of Fe^{2+} are added into solutions of BH_4^-. Let l, m and n denote the factors of the reactions shown in Equations 5–7 in the overall reaction for the formation of Fe–B UFAAP, the overall reaction will be the linear combination of these reactions. In this case, we obtained the following equations:

$$4l + 2m + 2.5n = N_{H_2,eq} \tag{8}$$

$$2m = N_{FeSO_4} \tag{9}$$

$$l + m + n = N_{KBH_4,eq} \tag{10}$$

when KBH_4 is in excess, where N_{FeSO_4} is the number of moles of $FeSO_4$ used and $N_{H_2,eq}$ and $N_{KBH_4,eq}$ are the moles of H_2 evolved and the moles of KBH_4 consumed, respectively, during the reaction up to the equivalent point. These values can be measured experimentally and then the factors l, m and n can be solved. Finally, the boron content in Fe–B samples can be calculated by the equation:

$$B\% = n/(2m + n) \times 100\% \tag{11}$$

Fig. 2 shows the pH versus time curves for the reaction of adding Fe^{2+} solutions with different concentrations at a constant rate ($7\ ml\ min^{-1}$) into BH_4^- solutions. Before the reactions, the solutions of KBH_4 had been adjusted to pH ≈ 12. The addition of $FeSO_4$ greatly decreased the pH since the reduction of Fe^{2+} occurred, which consumed OH^- (see Equation 6). The pH decreased more rapidly when more concentrated $FeSO_4$ solutions were used. With the decrease of pH due to the reduction of Fe^{2+}, the hydrolysis reaction of BH_4^- increased, which would increase pH of the reaction mixture (see Equation 5). Finally, the two reactions were balanced and the pH values were automatically maintained at some constant levels which depended on the concentration and addition rate of the $FeSO_4$ solutions. The pH levels were lower for the higher concentrated Fe^{2+} solutions, which might affect the boron content in the Fe–B products. After the Fe^{2+} solutions had been completely added, the excess BH_4^- continued to hydrolyse, resulting in a slight increase in the pH value. Since the added Fe^{2+} was immediately reduced to Fe, the amount of excess KBH_4, $N_{KBH_4,ex}$, can be obtained by measuring the amount of H_2 evolved after complete addition of the

$FeSO_4$ solution ($N_{KBH_{4,ex.}} = N_{H_{2,ex}}/4$). Then,

$$N_{KBH_{4,eq}} = N_{KBH_{4,to}} - N_{KBH_{4,ex}}$$

where $N_{KBH_{4,to}}$ is total amount of KBH_4 in solution.

For example, the curve b in Fig. 1 was obtained by adding in 8 min 56.50 ml of a solution containing 0.01598 mol of $FeSO_4$ into 200 ml of solution containing 0.05847 mol of KBH_4. The experimental data are as follows:

$$N_{FeSO_4} = 0.016 \text{ mol}$$

$$N_{KBH_{4,to}} = 0.058 \text{ mol}$$

$$N_{H_{2,eq}} = 0.133 \text{ mol}$$

$$N_{H_{2,ex}} = 0.070 \text{ mol}$$

$$N_{H_{2,to}} = 0.203 \text{ mol}$$

$$N_{KBH_{4,eq}} = N_{KBH_{4,to}} - N_{H_{2,ex}}/4 = 0.041 \text{ mol}$$

With these values, the numbers l, m and n in Equations (5–7) were calculated for this test to be 0.023, 0.008 and 0.010, respectively. Thus,

$$B\% = n/(2m + n) \times 100\% = 38.4\%$$

$$l/(l + m + n) \times 100\% = 56\%$$

$$BH_4^-/Fe^{2+} = (l + m + n)/2m$$

$$= 0.041/0.016 = 2.56$$

The boron content of this sample was found by ICP to be 38.0%, which is in good agreement with the calculated value of 38.4%, indicating that the mechanism is also valid for the reaction between Fe^{2+} and BH_4^- when Fe^{2+} was added. The hydrolysis of BH_4^- was about 56% in this case, similar to that for the reaction in acidic medium [15]. The ratio of BH_4^- to Fe^{2+} for the equivalent reaction was about 2.6, which is much higher than 1.9 for the reaction when BH_4^- was added.

Table I presents the results for Fe–B UFAAP samples prepared by the addition of $FeSO_4$ solutions into KBH_4 solutions. C_i is defined as the initial concentration of the $FeSO_4$ solutions [15]:

$$C_i = \frac{N_{FeSO_4}/t}{V_{KBH_{4,aq}} + V_{FeSO_{4,aq}}/t} \tag{12}$$

where $V_{KBH_{4,aq}}$ and $V_{FeSO_{4,aq}}$ are the volumes of the reaction solutions of KBH_4 and $FeSO_4$, respectively, and t is the time used for adding the $FeSO_4$ solution. It can be seen from Table I that the calculated boron contents in the samples prepared with different $FeSO_4$ concentrations are in good agreement with those determined by ICP, which further confirmed the reaction mechanism. The boron content decreased from ~38% to 31% at. with an increase in $FeSO_4$ concentration. It is obvious that the reaction in basic medium consumed more KBH_4 and produced Fe–B samples with higher boron contents compared to the reaction in acidic medium [15].

Fig. 3 shows the amount of H_2 evolved during the reactions with different concentrations of $FeSO_4$ solutions. The slopes of these lines are the rates of H_2 evolved during the reactions, which are taken as the overall reaction rates and are also listed in Table I. Fig. 4 shows the logarithmic plots of the rate of reaction for $H_2(r_{H_2})$ with respect to the C_i of $FeSO_4$ solutions, from which the Fe^{2+} order for the overall reaction was found to be first order. This may explain why the boron content in Fe–B samples decreases with an increase of $FeSO_4$ concentration. However, the pH level during the reaction may also play an important role in determining the boron content. The

TABLE I Experimental results for preparing Fe–B UFAAP by adding $FeSO_4$ solutions with different concentrations into solutions containing about 0.06 mol KBH_4. (Addition rate: 7 ml/min^{-1})

$C_i(FeSO_4) \times 10^4$ (mol/l^{-1})	B% calculated	B% analysed	$r_{H_2} \times 10^2$ mol per min
0.394	38.9	39.2	0.667
0.702	39.5	38.3	0.873
1.70	38.4	38.1	2.20
2.94	35.3	34.2	3.09
3.71	–	31.1	5.52

Note: C_i is defined by Equation 12.

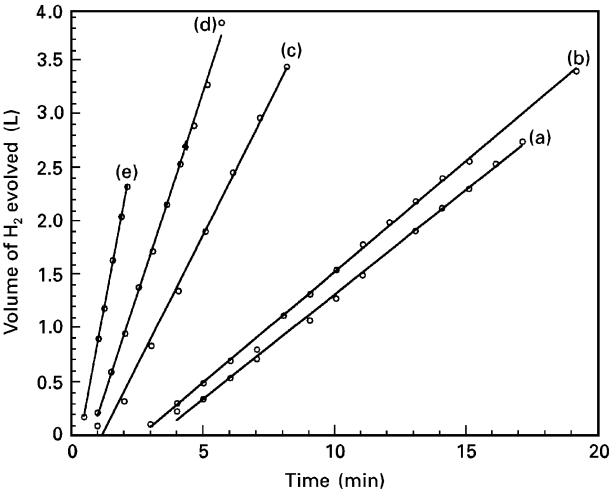

Figure 3 Rates of H_2 evolved during the reactions when $FeSO_4$ solutions with initial concentrations of (a) 3.94×10^{-5} mol per l, (b) 7.02×10^{-5} mol per l, (c) 1.70×10^{-4} mol per l, (d) 2.94×10^{-4} mol per l and (e) 3.71×10^{-4} mol per l were added into the KBH_4 solutions.

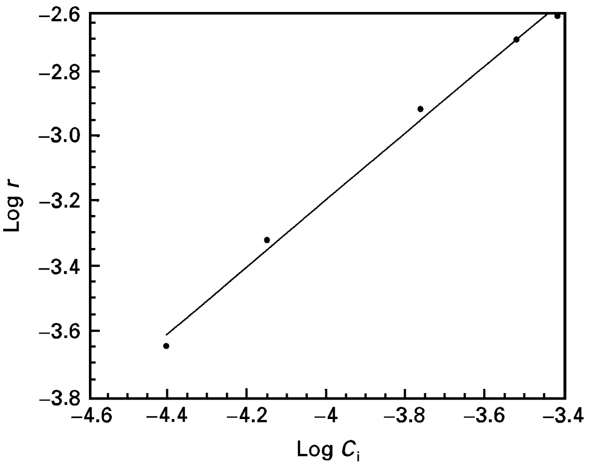

Figure 4 Logarithmic plots of reaction rates with respect to the initial concentration of $FeSO_4$ solutions.

TABLE II Effect of addition rate for adding 142 ml of a solution containing about 0.02 mol $FeSO_4$ into a 200 ml of solution containing about 0.06 mol KBH_4

N_{FeSO_4} (mol)	Addition time (min)	Boron content (at %)
0.019 99	0.12	13.9
0.020 01	2.0	25.5
0.019 99	5.0	28.4
0.020 01	10.0	34.1
0.020 00	20.0	38.3
0.020 00	30.0	37.5
0.020 00	40.0	36.9
0.020 00	60.0	35.5

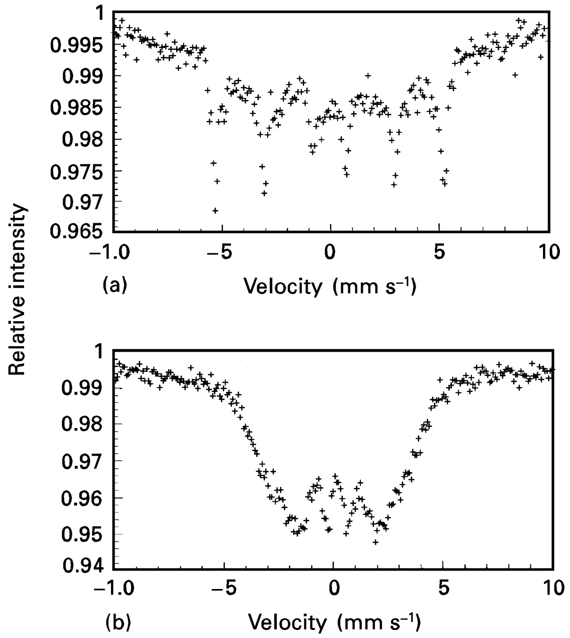

Figure 5 Room temperature Mössbauer spectra of Fe–B samples prepared when $FeSO_4$ solutions were added into KBH_4 solutions in (a) 0.12 min and (b) 20 min.

pH level of the reaction (see Fig. 1) and the boron content were much higher for the samples produced by the addition of Fe^{2+} than for those produced by the addition of BH_4^-, which may imply that the reaction at higher pH produced samples with a higher boron content. This argument is consistent with the results displayed in Fig. 2 and listed in Table I, which show that with an increase of $FeSO_4$ concentration, the pH level of the reaction and the boron content for the samples decreased.

The effect of the addition rate of $FeSO_4$ solution was also investigated. The results as listed in Table II indicate that the boron content increased substantially from 13.9–38.3% with an increase in the addition time from 0.12–20 min and then decreased slowly from 38.3–35.5% in addition times of 30–60 min. These results demonstrate that the boron content may be controlled over a large range by varying the concentration and addition rate of the $FeSO_4$ solutions.

Room temperature Mössbauer spectra were recorded for the samples prepared with different addition rates of the $FeSO_4$ solutions. Fig. 5(a and b) displays the Mössbauer spectra for the samples prepared with the addition times of 0.12 and 20 min as listed in Table II. The sample produced with the very fast addition rate (0.12 min) exhibits a Mössbauer spectrum (Fig. 5a) showing a component with a sharp sextet which can be assigned to α-Fe according to its hyperfine field (2.626×10^6 Am^{-1}), indicating that a large amount of the iron in this sample was in crystalline form. The Mössbauer spectrum of the sample prepared with an addition time of 20 min (Fig. 5b) shows a broadened sextet typical of an amorphous state for the iron [14]. Other samples prepared with addition times from 2–60 min display similar Mössbauer spectra to that shown in Fig. 5b, indicating that these samples were in an amorphous state.

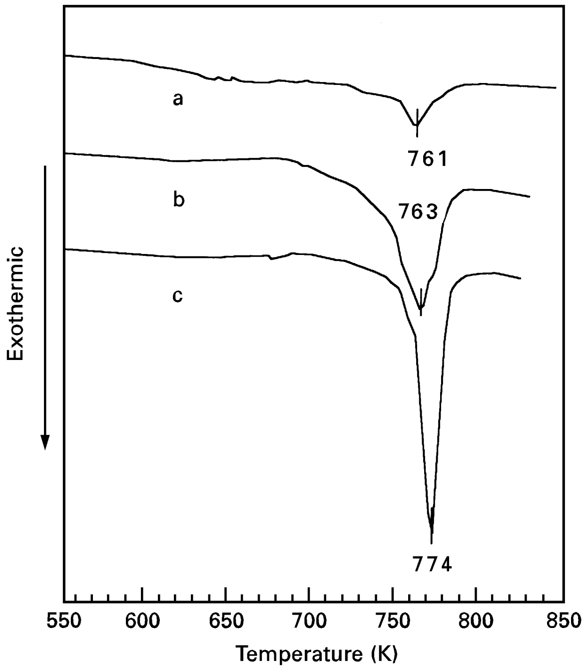

Figure 6 Differential scanning calorimetric profiles of the Fe–B samples prepared when $FeSO_4$ solutions were added into KBH_4 solutions in (a) 0.12 min, (b) 2 min and (c) 10 min.

Fig. 6 shows the DSC profiles of the Fe–B samples prepared with different addition rates of the $FeSO_4$ solutions. The samples with addition times less than 2 min exhibited broadened exothermic peaks, which may imply a distribution of local structures with the iron atoms being surrounded by different numbers of boron atoms [19]. The sample with a fast addition rate (0.12 min) only showed a small exothermic peak (Fig. 6 curve a), consistent with the Mössbauer result which showed that some iron in this sample was crystalline. The samples prepared with addition times longer than 10 min exhibited a similar sharp exothermic peak around 774 K as shown in Fig. 6 curve c. These samples had boron contents higher than 34% and exhibited higher crystallization temperatures than those samples with boron contents lower than 29% [14].

4. Conclusions

In summary, the following conclusions can be reached from the results obtained in the present study and also references [3, 14, 15]:

(1) The ways of mixing $FeSO_4$ and KBH_4 solutions greatly affects the boron content and properties of the Fe–B UFAAP samples produced. The boron content of the Fe–B samples prepared with the addition of $FeSO_4$ into KBH_4 can be as high as 39% whereas the boron content is limited to 29% in the samples prepared with the addition of KBH_4 into $FeSO_4$.

(2) The mixing rate of the two reactant solutions also significantly influences the boron content. In either case, i.e., addition of KBH_4 into $FeSO_4$ or *vice versa*, the boron content increases from 10–29% or from 13.9–39% with an increase in the addition time from 0.12–30 min.

(3) The concentration of the reactant solutions also influences the boron content. In either case, the boron content increases with a decrease in the concentration of the solution being added during the reaction.

(4) The reactions carried out with both addition directions follow the same mechanism as expressed by the three independent reactions:

$$BH_4^- + 2H_2O = BO_2^- + 4H_2\uparrow \qquad (5)$$

$$BH_4^- + 2Fe^{2+} + 4OH^- = 2Fe + BO_2^- + 2H_2O + 2H_2\uparrow \qquad (6)$$

$$BH_4^- + H_2O = B + OH^- + 2.5H_2\uparrow \qquad (7)$$

The ratio of the reactions shown in Equations 6 and 7 determines the boron content in Fe–B samples and may be widely varied by controlling reaction conditions. The reaction proceeds at a constant pH level throughout the reaction because reactions 5 and 7 create while reaction 6 consumes OH^- groups in both cases. However, the reaction proceeds at basic and acidic media, respectively, for the addition of $FeSO_4$ into KBH_4 and *vice versa*. This may explain why the way of mixing the reactants greatly influences the boron content of the produced Fe–B samples.

(5) Finally, when the two reaction solutions were mixed rapidly (in several seconds) for the addition of KBH_4 into $FeSO_4$ and *vice versa* or when the two reactant solutions were mixed (even slowly) in a "Y-junction", low boron content samples were obtained which were found to be at least partially crystalline.

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References

1. J. VAN WONTERGHEM, S. MØRUP, C. J. W. KOCH, S. W. CHARLES and S. WELLS, *Nature* **322** (1986) 622.
2. S. G. KIM and J. R. BROCK, *J. Coll. Interf. Sci.* **116** (1987) 431.
3. L. YIPING, G. C. HADJIPANAYIS, C. M. SORENSEN and K. J. KLABUNDE, *J. Magn. Magn. Mater.* **79** (1989) 321.
4. S. LINDEROTH, S. MØRUP, A. MEAGHER, J. LARSEN and M. D. BENTZON, *ibid.* **81** (1989) 138.
5. S. LINDEROTH, S. MØRUP and M. D. BENTZON, *ibid.* **83** (1990) 457.
6. C. A. BROWN and H. C. BROWN, *J. Amer Chem. Soc.* **85** (1963) 1003.
7. *Idem*, *ibid.* **85** (1963) 1005.
8. C. A. BROWN, *J. Org. Chem.* **35** (1970) 1900.
9. R. C. WADE, D. G. HOLAH, A. N. HUGHES and B. C. HUI, *Catal. Rev. Sci. Engng.* **14** (1976) 211.
10. JIANYI SHEN, Z. LI, Q. ZHANG, Y. CHEN, Q. BAO and Z. LI, Proceedings of 10th International Congress on Catalysis, Budapest, Hungary, 1992. Edited by L. Guczi *et al.* (Elsevier, 1993) p. 2193.
11. S. WELLS, S. W. CHARLES, S. MØRUP, S. LINDEROTH, J VAN WONTERGHEM, J. LARSEN and M. B. MADSEN, *J. Phys.: Condens. Matter* **1** (1989) 8199.
12. S. LINDEROTH and S. MØRUP, *J. Appl. Phys.* **67** (1990) 4472.
13. *Idem*, *ibid.* **69** (1991) 5256.
14. JIANYI SHEN, Z. LI, Y. FAN, Z. HU and Y. CHEN, *J. Solid State Chem.* **106** (1993) 493.
15. JIANYI SHEN, Z. LI, Q. YAN and Y. CHEN, *J. Phys. Chem.* **97** (1993) 8504.
16. JIANYI SHEN, Z. LI and Y. CHEN, *J. Mater Sci. Lett.* **13** (1994) 1208.
17. G. C. HADJIPANAYIS, Z. X. TANG, S. GANGOPADHYAY, L. YIPING, C. M. SORENSEN, K. J. KLABUNDE, A. KOSTIKAS and V. PAPAEFTHYMIOU, in "Studies of Magnetic Properties of Fine Particles", edited by J. L. Dormann and D. Fiorani, (Elsevier Science Publishers B.V. North-Holland, 1992) p. 35.
18. R. L. PECSOK, *J. Amer Chem. Soc.* **75** (1953) 2826.
19. JIANYI SHEN, ZHENG HU, QINGHONG ZHANG, LIFENG ZHANG and YI CHEN, *J. Appl. Phys.* **71** (1992) 5217.

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