Low temperature synthesis of nanocrystalline Co₂B

Pei-jun CAI,[†] Hao WANG, Li-hua LIU and Li ZHANG

School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu, P. R. China

Nanocrystalline cobalt boride (Co₂B) has been successfully synthesized by the reaction of CoCl₂ with NaBH₄ in the temperature range of 500–600°C in an autoclave. Characterized by X-ray powder diffraction (XRD), transmission electron micrographs (TEM), and Raman spectra, the composition and morphology of the products were confirmed. The mechanism for the formation of crystalline Co₂B was proposed. This work contributes one facile method for preparing metallic borides.

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1. Introduction

Research on cobalt borides has been active in the past decade because of their catalytic and magnetic properties. They have wide range of potential applications: catalysts,^{1,2)} high-density magnetic recording media and ferrofluids.³⁾ Cobalt borides were reported as important catalysts for various reactions such as hydrogenation, deselenization and desulfurization.^{4,5)} The catalytic and magnetic properties of cobalt borides depend crucially on their shape or size.^{6,7)} Ultrafine amorphous cobalt borides powders have been prepared by chemical reduction of Co²⁺ with borohydride in aqueous solution.^{8,9)} Through high temperature treatment (500–900°C), cobalt borides coexisting with metallic cobalt were obtained.¹⁰⁾ Nanosize amorphous cobalt boride was obtained by the reduction of cobalt (2-ethyl hexyl) sulfosuccinate, Co(AOT)₂, by sodium borohydride either in reverse micelles or in adiphase system.¹¹⁾ W. Tang reported Preparation and performance of cobalt boride interlayer.¹²⁾ Thermal liquid-solid metathesis reaction are attracting increasing interest due to its convenience operate. G. N. Makarenko and co-workers studied the characteristic features of synthesis of cobalt borides by boron carbide reduction of oxides in the temperature range 1100 to 1900 K under vacuum.¹³⁾

In this letter, we present one novel method to prepare nanocrystalline Co₂B by the reaction of CoCl₂ and NaBH₄ in the low temperature range of 500–600°C in an autoclave. To the best of our knowledge, no reports on such work are found in the literature. The reaction can be described as follows:

2. Experimental procedures

All the reagents used were of analytical-grade purity (purchased from Shanghai Chem. Co.). In a typical procedure, an appropriate amount of 0.04 mol CoCl₂ and 0.01 mol NaBH₄ powder was put into a quartz tube, which was placed into a stainless steel autoclave with the volume of 60 mL. Then, the autoclave was sealed under Ar atmosphere and heated at 500, 550 and 600°C for 12 h, followed by naturally cooling to room temperature. The products were washed with distilled water and absolute ethanol several times to remove the impurities. The final

products were vacuum-dried at 60°C for 4 h. Black powders were obtained.

The obtained samples were characterized by X-ray powder diffraction (XRD) on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology of nanocrystalline Co₂B was examined from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. The Raman spectroscopy analysis was carried out on a LABRAM-HR Confocal Laser Micro-Raman Spectrometer at room temperature.

3. Results and discussion

Figure 1 shows the XRD patterns of the sample prepared at 500, 550 and 600°C for 10 h. All reflections can be indexed as Tetragonal Co₂B with lattice constants $a = 5.001$ and $c = 4.232 \text{ \AA}$, which are close to the reported values of Tetragonal

Fig. 1. XRD patterns of the Co₂B sample.

[†] Corresponding author: P.-J. Cai; E-mail: peijuncaicai@hotmail.com

Fig. 2. (a–c) TEM images of the samples prepared at: (a) 450°C for 10 h (SAED pattern inserted); (b) 500°C for 10 h; (c) 600°C for 10 h, and (d) SAED pattern of the nanocrystalline Co_2B .

Co_2B ($a = 5.006 \text{ \AA}$, $c = 4.212 \text{ \AA}$) (JCPDS No. 75-1063). No noticeable peaks of impurities can be detected in the XRD patterns.

The particle distribution and the microstructure of Co_2B were investigated by TEM as shown in Fig. 2. It can be noticed that, a homogeneous distribution of the nanoparticles prevails over a wide range of the sample. Also, it is made up of small spheres or faceted particles. The influences of reaction temperature on the formation of the nanocrystalline Co_2B were investigated. In the present preparation process, it is found that the reaction temperature plays important role in the formation of Co_2B . For Co_2B nanoparticles, no Co_2B could be obtained if the temperature is below 450°C. SAED pattern of one typical solid prepared at the temperature of 450°C was inserted in Fig. 2a, no obvious polycrystalline rings were detected, which indicated that low crystalline or amorphous materials is produced. An optimum reaction temperature for the nanocrystalline Co_2B was about 500–600°C. As the temperature was higher than 500°C, the crystallinity of Co_2B increased evidently (as shown in Figs. 2b–c). Varying the treatment time between 10 and 24 h at 500°C did not significantly affect the crystallinity or the yield of Co_2B , indicating a rapid reaction between CoCl_2 and NaBH_4 once the reaction is initiated. The rough molar yield of Co_2B is 90%. Figure 2d shows the SAED pattern of the nanocrystalline Co_2B sample prepared at 500°C for 10 h. The polycrystalline rings [(110) and (200)] confirm the XRD result.

Figure 3 shows the Raman spectra of the as-prepared Co_2B sample at room temperature. Two peaks at 1429.2 and 2677.7 cm^{-1} could be observed clearly, which is attributed to Raman

Fig. 3. Raman spectrum of the samples.

active modes E_g and T_{2g} for Co_2B , respectively. It is found that the full width at half maximum of this Raman peak is about 300 cm^{-1} . This anomalously large line width for Co_2B Raman peak may be due to the existence of strong electron-phonon coupling in Co_2B .¹⁴⁾

As to the formation mechanism of Co_2B , we speculate that when the temperature increasing up to 500°C, the NaBH_4 begin to decompose generating gaseous BH_3 and NaH .¹⁵⁾ The gaseous BH_3 could react with CoCl_2 to produce Co_2B , gaseous HCl and H_2 . The produced HCl is reduced by NaH to form NaCl and H_2 . One feature of this synthesis route is the high pressure in the autoclave, coming from the produced BH_3 and H_2 . The high pressure makes the crystalline Co_2B form at relatively low temperature. The possible formation process of Co_2B could be illustrated as following.

In comparison with previous routes, the present route allows for the rapid formation of Co_2B at a very low temperature by using less costly raw materials through a simple process. This method may be extended to synthesis other borides.

4. Conclusions

In summary, the ultrafine Co_2B powder was successfully synthesized using CoCl_2 and NaBH_4 as the reactants in the temperature range of 500–600°C. The products mainly consisted of hexagonal phase particles with an average size of 80 nm. This route allows for the facile formation of Co_2B at a low temperature, and may be extended to synthesis of other borides.

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References

- 1) H. X. Li, X. F. Chen, M. H. Wang and Y. P. Xu, *Appl. Catal., A*, 225, 117–130 (2002).
- 2) J. C. Walter, A. Zurawski, D. Montgomery, M. Thornburg and S. Revankar, *J. Power Sources*, 179, 335–339 (2008).

- 3) J. Legrand, A. Taleb, S. Gota, M. J. Guittet and C. Petit, *Langmuir*, **18**, 4131–4137 (2002).
- 4) Y. Z. Chen, S. W. Wei and K. J. Wu, *Appl. Catal., A*, **99**, 85–96 (1993).
- 5) E. Lugowska, *Analyst*, **122**, 1559–1568 (1997).
- 6) M. L. Billias, I. A. Châtelain and W. A. de Heer, *Science*, **265**, 1682–1684 (1994).
- 7) C. Petit and M. P. Pileni, *J. Magn. Magn. Mater.*, **166**, 82–90 (1997).
- 8) H. X. Li, X. F. Chen, M. G. Wang and Y. P. Xu, *Appl. Catal., A*, **225**, 117–130 (2002).
- 9) A. Corrias, G. Ennas, A. Musinu, G. Marongiu and G. Paschina, *Chem. Mater.*, **5**, 1722–1726 (1993).
- 10) Y. Z. Chen and K. J. Wu, *Appl. Catal.*, **78**, 185–197 (1991).
- 11) H. Y. Ma, G. Z. Li, J. P. Zhan, Q. Shen and X. W. Wang, *J. Dispersion Sci. Technol.*, **19**, 511–520 (1998).
- 12) W. Tang, S. Wang and F. Lu, *Diamond Relat. Mater.*, **9**, 1744–1748 (2000).
- 13) G. N. Makarenko, S. P. Gordienko, V. B. Fedorus, É. V. Marek and I. I. Timofeeva, *Powder Metall. Met. Ceram.*, **43**, 192–195 (2004).
- 14) G. Mavel, J. Escard, P. Costa and J. Castaing, *Surf. Sci.*, **35**, 109–116 (1973).
- 15) A. G. Ostroff and R. T. Sanderson, *J. Inorg. Nucl. Chem.*, **4**, 230–231 (1957).