

A mild solvothermal route to nanocrystalline titanium diboride

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Abstract

Titanium diboride (TiB₂) has been synthesized via a benzene-thermal reaction of metallic sodium with amorphous boron powder and titanium tetrachloride at 400 °C in an autoclave; the temperature was much lower than that of traditional methods. The X-ray diffraction (XRD) pattern can be indexed with the hexagonal cell of TiB₂ and the lattice constants $a=3.027$ and $c=3.228$ Å. X-ray photoelectron spectroscopy (XPS) results show the mole ratio of Ti:B as 1:1.766. Transmission electron microscope (TEM) images indicate that the average particle size is in the range of 15–40 nm in diameter.

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1. Introduction

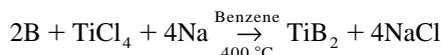
Borides of transition metals have attracted considerable interest for their various unique properties. Among these intermetallic compounds, TiB₂ has a high melting point, high hardness and strength, excellent wear and corrosion resistance, which surpass that of titanium nitride and carbide [1–3]. Titanium diboride is an important material in diecasting and dry cutting industry for wear, corrosion and erosion protection [4,5]. As it has a high temperature stability and good electrical conductivity, titanium diboride is also a promising interconnection material for integrated circuits [6].

Traditionally, titanium diboride powder was prepared by a variety of high temperature methods [7], such as the direct reactions of titanium, its oxide or hydrides, with elemental boron over 1000 °C; carbothermal reduction of titanium oxide and boron oxide; or hydrogen reduction of boron halides in the presence of the metal or its halides. Recently, electrochemical syntheses [8,9] and solid-state reactions [3,10–12] have been developed for preparing titanium diboride. However, these methods generally cannot lead to nano-sized products.

Previously, Bates and co-workers [13] have prepared nanocrystalline TiB₂ of 5–100 nm via an initial solution-

phase reaction of NaBH₄ and TiCl₄, followed by annealing the obtained amorphous precursor at 900–1100 °C. Axelbaum and co-workers [14,15] have developed a gas-phase combustion process that can directly yield unagglomerated, low-oxygen TiB₂ nanoparticles by the reaction of sodium vapor with TiCl₄ and BCl₃. However, the products were contaminated with metallic titanium and titanium oxide.

Recently, we have developed a novel route to nanocrystalline titanium diboride via a solvothermal reaction of metallic sodium with amorphous boron powder and TiCl₄ at 400 °C. It can be described as follows,



where TiB₂ formation and crystallization proceeded synchronously. In forming nanocrystalline TiB₂, active nascent titanium was generated in reducing TiCl₄ by metallic sodium. The titanium reacted with boron forming titanium diboride. Benzene serves as reaction medium to control reaction speed and particle size. By confining the reaction within an anaerobic environment, the product was free of oxide impurity. However, sample surface oxidation may occur during the purification process.

2. Synthesis and purification procedure

Firstly, 1 g of amorphous boron powder (2 μm, Merck KGaA), 25 ml of benzene and 5 ml of liquid analytical

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pure TiCl_4 were placed in a quartz tube. The excessive metallic sodium (about 4.5–5.0 g) was freed of kerosene by washing with benzene. Then, the sodium was added in the quartz tube. Finally, the quartz tube was put in a stainless steel autoclave and sealed under argon atmosphere. The autoclave has a capacity of some 50 ml. Before sealing the autoclave, approximately 10 ml of benzene was put into the autoclave to balance heat and pressure. The autoclave was heated at 400 °C for 8 h, followed by naturally cooling to room temperature outside the furnace. The obtained sample from the quartz glass tube was washed several times with absolute ethanol, distilled water and acetone to remove impurities. The final product was vacuum-dried at 60 °C for 12 h, and 2.145 g of gray powder product was obtained.

The gray powder product was analyzed by X-ray photoelectron spectroscopy (XPS) using an ESCALAB MK2 with aluminium $K\alpha$ rays, powder X-ray diffraction (XRD) on an X-ray diffractometer (Rigaku rA) using $\text{Cu } K\alpha$ radiation (wavelength $\lambda = 1.54178 \text{ \AA}$), and transmission electron microscopy (TEM) with a Hitachi 800 transmission electron microscope.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared TiB_2 sample. All the seven peaks at d -spacing of 3.2274, 2.6217, 2.0350, 1.6133, 1.5131, 1.3747, 1.2147 Å were indexed as hexagonal TiB_2 [(001), (100), (101), (002), (110), (102), (021)]. The rms error of fit was 9.334×10^{-5} , with the lattice constants $a = 3.027$ and $c = 3.228$ Å in good agreement with $a = 3.030$ and $c = 3.230$ Å (JCPDS card# 35-741).

The wide-scan XPS spectrum of the as-prepared TiB_2 sample is shown in Fig. 2. It shows that the sample surface consists of titanium, boron, carbon and oxygen, with binding energies of $\text{Ti}3p$, $\text{Ti}3s$, $\text{B}1s$, $\text{C}1s$, $\text{Ti}2p_{3/2}$, $\text{Ti}2p_{1/2}$,

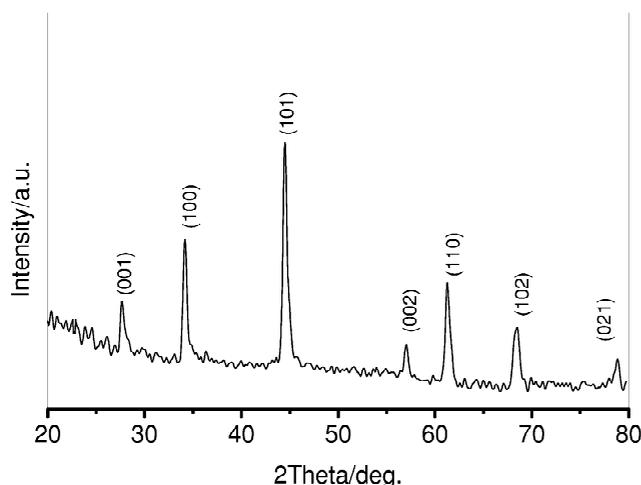


Fig. 1. XRD pattern of the as-prepared TiB_2 sample.

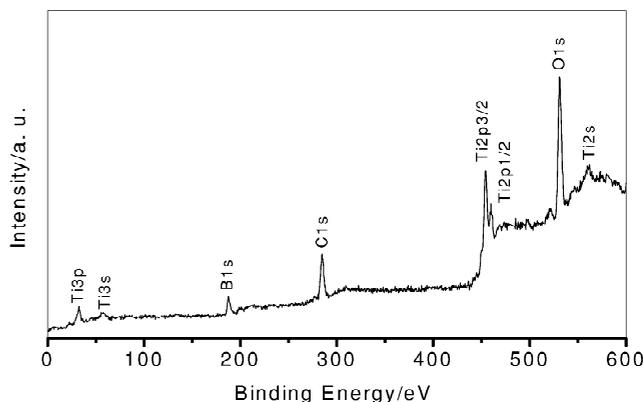


Fig. 2. Wide-scan XPS spectrum of the as-prepared TiB_2 sample.

$\text{O}1s$ and $\text{Ti}2s$ at 32.20, 58.83, 187.68, 285.00, 454.42, 460.00, 530.95 and 561.29 eV, respectively. The $\text{B}1s$ peak at 187.68 eV indicates boron combined with titanium forming titanium boride; this corresponds to the $\text{Ti}2p_{3/2}$ at 454.42 eV, which was considered as the titanium bonding with boron forming TiB_2 [16]. As the reaction is strongly exothermic, the local temperature may temporarily become higher than 400 °C. Therefore, the carbon may come mainly from carbonization of small quantities of benzene and sample surface adsorption. The $\text{O}1s$ peak was not very symmetric, indicating TiB_2 surface oxidation as well as oxygen adsorption. The mole ratio of $\text{Ti}:\text{B}$ was calculated as 1:1.766, slightly less than that of TiB_2 . It may be due to surface enrichment of titanium induced by surface oxidation.

A transmission electron microscope (TEM) image and selected area transmission electron diffraction (TED) pattern are shown in Fig. 3. In Fig. 3a, the material exhibits slightly agglomerated particle morphology. The primary particle size was estimated in the range of 15–40 nm in diameter. Some amorphous carbon may cling to and disperse between the TiB_2 primary particles. The TED pattern in Fig. 3b confirms the nanocrystallinity of TiB_2 , in which the diffraction ring diameters and intensities again correspond well to the hexagonal TiB_2 phase.

4. Conclusion

In summary, nanocrystalline TiB_2 of 15 to 40 nm with the hexagonal cell has been successfully prepared via a benzene-thermal synthetic route by the reaction of metallic sodium with amorphous boron powder and titanium tetrachloride at 400 °C. This study demonstrates that the solvothermal synthesis can be a mild method for preparing titanium diboride nanomaterials. In a further study, efforts will be made to research a better understanding of the reaction mechanism and to control the reaction kinetics.

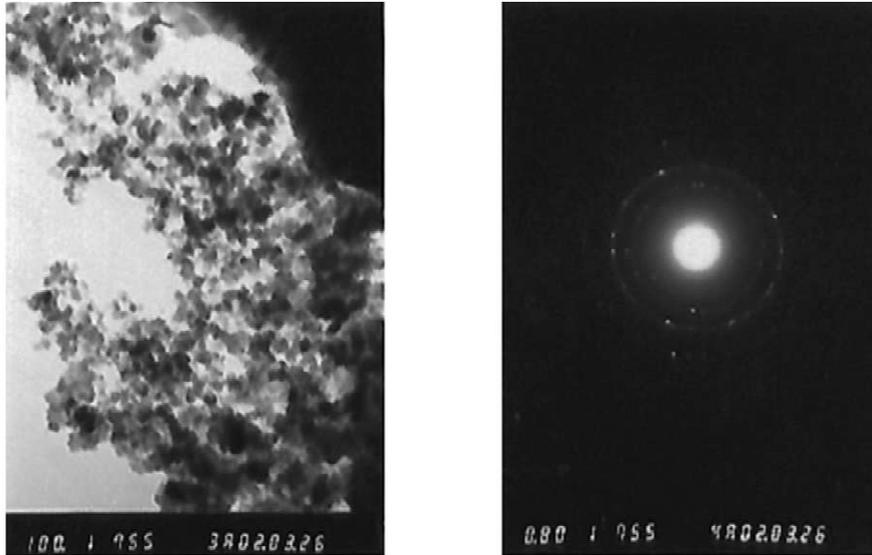


Fig. 3. TEM (a, scale bar, 150 nm) and TED (b) images of the as-prepared TiB_2 sample.

Acknowledgements

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