Preparation of titanium diboride powders from titanium alkoxide and boron carbide powder

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Abstract.   Titanium diboride powders were prepared through a sol–gel and boron carbide reduction route by using TTIP and B_4C as titanium and boron sources. The influence of TTIP concentration, reaction temperature and molar ratio of precursors on the synthesis of titanium diboride was investigated. Three different concentrations of TTIP solution, 0·033/0·05/0·1, were prepared and the molar ratio of B_4C to TTIP varied from 1·3 to 2·5. The results indicated that as the TTIP concentration had an important role in gel formation, the reaction temperature and B_4C to TTIP molar ratio showed obvious effects on the formation of TiB_2. Pure TiB_2 was prepared using molar composition of $Ti : B_4C = 1 : 2·3$ and the optimum synthesis temperature was 1200°C.

Keywords.   Titanium diboride; sol–gel; boron carbide; reduction; TTIP.

1. Introduction

Titanium diboride is a hard refractory material with a high melting point, low electrical resistivity and high thermal conductivity (Kim and McMurtry 1985). In addition, sintered TiB_2 is resistant to oxidation up to 1100°C and chemically stable in many harsh, corrosive environments (Greenwood 1973). TiB_2 has also low solubility and is wetted by most molten metals up to 1000°C. The combination of these properties makes TiB_2 a very interesting engineering ceramic material which can be used as ballistic armor, coatings for cutting tools (Funk *et al* 1973), crucibles and electrodes in metal refining equipments such as aluminum reduction cells (Murata and Miccioli 1971).

TiB_2 can be prepared by carbothermic reduction of mixed oxides of boron and titanium, reduction of titanium oxide by boron carbide and carbon, reduction of mixed oxides by metals like aluminum, silicon, magnesium, etc. TiB_2 can also be synthesized from the elements by heating, mechanical alloying or self-propagating high temperature synthesis (SHS) (Matkovich 1977; Radev 1996; Weimer 1997; Ge and Ye 2002; Hwang 2002; Krishnarao and Subrahmanyam 2003).

Sol–gel technique has been widely used for the manufacturing of nano-phased powders such as metal oxides and ceramics. In the process, reactive metal precursors were initially hydrolyzed, followed by condensation and polymerization reactions. Metal alkoxides are metal-organic compounds having an organic ligand attached to a metal or metallic atom. Because of the synthesis from atomic or molecular precursors, sol–gel technique can give better control of particle size and homogeneity in particle distribution (Cushing 2004; Tjong and Chen 2004). This work demonstrates the formation of TiB_2 by sol–gel method using a mixture of titanium tetra isopropoxide (TTIP) and boron carbide as precursor materials.

2. Experimental

The starting materials for preparation of TiB_2 were synthesized by hydrolyzing titanium tetra isopropoxide ($Ti[OCH(CH_3)_2]_4$, 97% purity, Alfa Aesar) with four molar equivalents of distilled water in IPA solvent (Isopropyl Alcohol, C_6H_5OH, 99% purity) under vigorous stirring. Three different TTIP concentrations in IPA were prepared: 0·033, 0·050 and 0·1 M. The $B_4C : Ti : H_2O$ molar ratio of the starting material was $x : 1 : 4$, where x varied from 1·3 to 2·5. The resulting dark suspension was stirred for 105 min at room temperature, the volatile components were removed under vacuum at 140°C. The powder then was heat treated at 900–1200°C in a graphite crucible in 1 atm argon. The phase analysis of the synthesized powders was carried out by an X-ray diffractometer (Simens D500, Germany) with $CuK\alpha$ ($\lambda = 1·540598$ Å) radiation. Morphology of the powders was analyzed by scanning electron microscope (Camscan MV2300, 27.0 kV).

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3. Results and discussion

Science alkoxides of transition metals are highly reactive to water, TTIP precursor can readily react with water via the following reaction to form titanium hydroxide (Levin 1999). According to the high positive charges on the metal of the complex, the rate of hydrolysis is very rapid and nonstable titanium hydroxide converted to titanium dioxide as the reaction proceeded in time
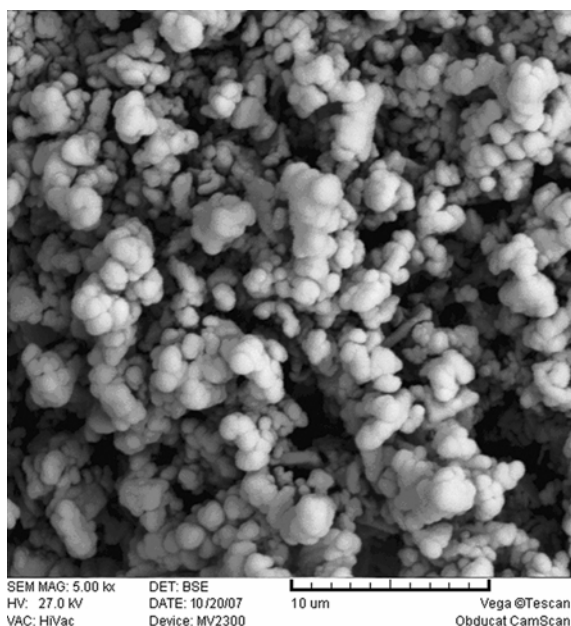
$$Ti[OCH(CH_3)_2]_4 + 4H_2O = Ti(OH)_4 + 4C_3H_7OH, \quad (1)$$

$$Ti(OH)_4 = TiO_2 + 2H_2O. \quad (2)$$
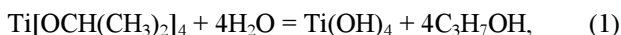
In the case of a solution containing a given concentration of precursors, when hydrolysis occurred, the content of the $Ti(OH)_4$ gradually increased with time. When the solution reached its minimum concentration for nucleation, nuclei appeared and grew. This caused the solute concentration to level off and to start decreasing. If the concentration of solute falls below the minimum level for nucleation, growth takes place exclusively.
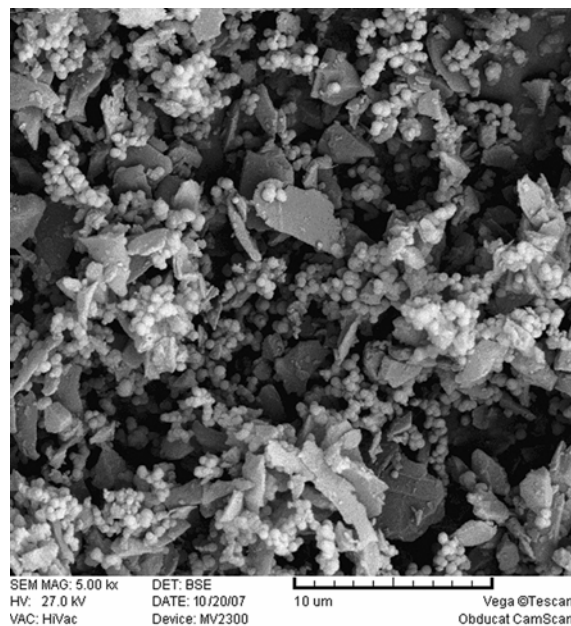
The finer particles of $Ti(OH)_4$ resulted from the solution containing 120 TTIP in the range of 0·050–0·10 M. Since heterogeneous nucleation is energetically favoured, in general, this process starts at a lower concentration than that of homogeneous nucleation. The surface of the B_4C powders, which were dispersed in the solution, may act as nucleation sites. In the case of concentration which was higher than the minimum value for homogeneous nucleation, the $Ti(OH)_4$ phase nucleated separately on the B_4C powder surfaces, resulting in a mixture of B_4C and

$Ti(OH)_4$ particles. As a result, the concentration of 0·050–0·10 M TTIP must have been in the range for homogeneous nucleation.

Figure 1 shows the morphology of the sample with the concentration of TTIP in maximum value, 0·1 M. Obviously, the homogenous nucleation of $Ti(OH)_4$ phase occurred and the $Ti(OH)_4$ phase nucleated separately from the B_4C powder surfaces, so a mixture of B_4C and

Figure 2. SEM image of homogenous and heterogeneous nucleation of spherical $Ti(OH)_4$ particles that were mainly formed on the B_4C powder surfaces for 0·05 M TTIP.

Figure 1. SEM image of homogenous nucleation of $Ti(OH)_4$ phase and mixture of B_4C and $Ti(OH)_4$ particles for 0·1 M TTIP.
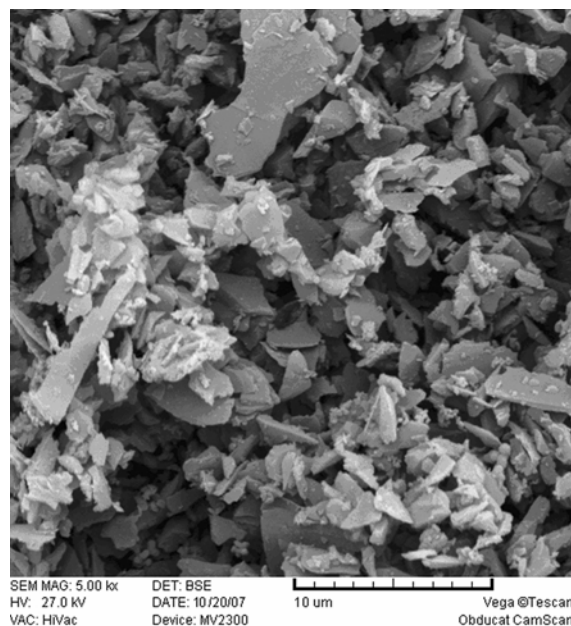
Figure 3. The low TTIP concentration did not cause nucleation of spherical $Ti(OH)_4$ powders during hydrolyze process.

$Ti(OH)_4$ particles were observed. As the concentration of TTIP decreased to 0·05 M, the nucleation of $Ti(OH)_4$ phase was partly homogenous and partly heterogeneous and spherical $Ti(OH)_4$ particles mainly formed at the surface of the B_4C powders (figure 2). When the concentration of TTIP was less than 0·05 M, formation of spherical $Ti(OH)_4$ particles were not observed (figure 3).

As indicated in figure 4, the spherical particle size of titanium hydroxide was less than 100 nm.

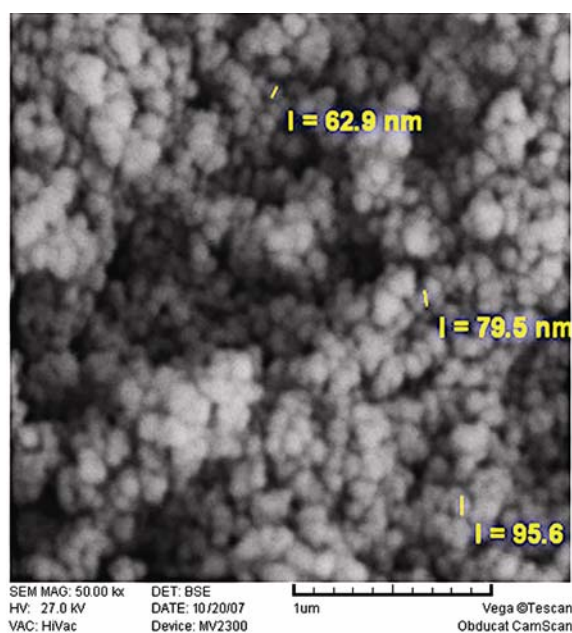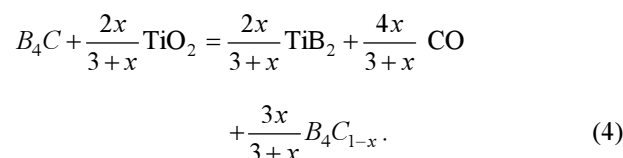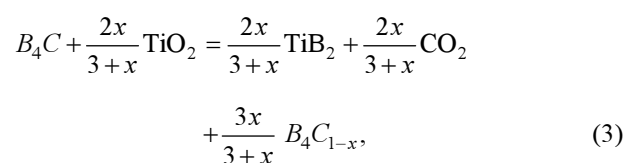TiO_2 can be reduced by carbon in the boron carbide phase according to the following reactions

$$B_4C + \frac{2x}{3+x} TiO_2 = \frac{2x}{3+x} TiB_2 + \frac{2x}{3+x} CO_2$$
$$+ \frac{3x}{3+x} B_4C_{1-x}, \qquad (3)$$

$$B_4C + \frac{2x}{3+x} TiO_2 = \frac{2x}{3+x} TiB_2 + \frac{4x}{3+x} CO$$
$$+ \frac{3x}{3+x} B_4C_{1-x}. \qquad (4)$$

The equilibrium parameters for the reduction of TiO_2 by carbon originating from the boron carbide phase and thermodynamic analysis were calculated and reported by Levin *et al* (1999). The amounts of TiB_2 in the final product and consumption of all reactants depend obviously on the amount of TiO_2 that was added, here TTIP, the source of TiO_2.

In the XRD pattern of the sample with the B_4C to TTIP molar ratio of 1·3, only the TiO_2 peaks and main peaks of TiB_2 can be seen. Analysis of these peaks by X-powder software showed 5·6%wt. of B_4C and 16·8%wt of TiB_2.

Figure 4. SEM image of $Ti(OH)_4$ particles and its particle size after hydrolyze process.

Figure 6. Effects of B_4C to TTIP molar ratio on weight percent of TiO_2 and TiB_2 heat treated at 1100°C.

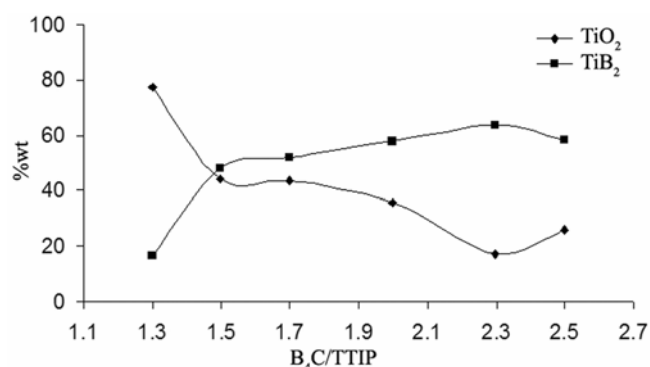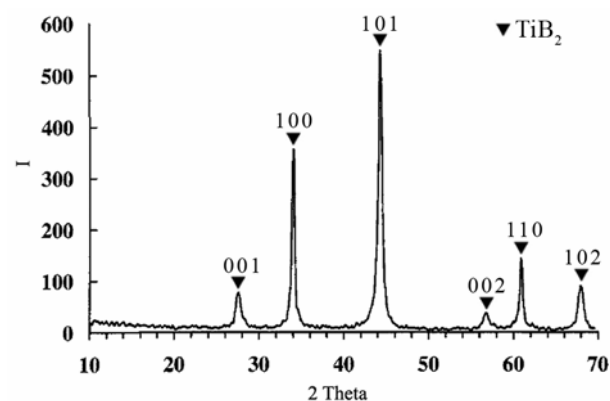**Figure 5.** XRD patterns of TiB_2 synthesized at 1100°C with various molar ratio of B_4C to TTIP.

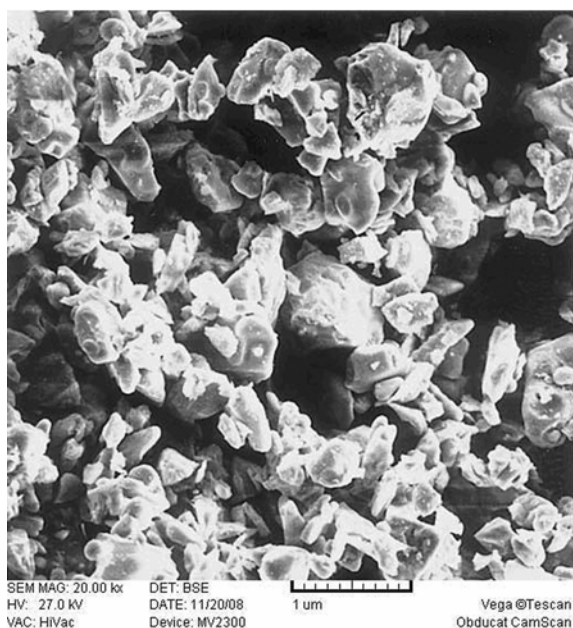**Figure 7.** XRD pattern of the sample with the molar ratio of 2·3 heat treated for 1 h at 1200°C.

Figure 8. Morphology of TiB_2 particles of the sample with the molar ratio of 2·3 heat treated for 1 h at 1200°C.

This result suggested that there was not enough amount of boron carbide to fully react with titanium dioxide, so all B_4C and appropriate amount of TiO_2 reacted to form TiB_2.

Increasing the molar ratio of B_4C to TTIP to 1·5, resulted in 33% more TiO_2. As the B_4C to TTIP molar ratio increased, the diffraction peaks of titanium diboride increased along with a decrease of titanium dioxide peaks. When the ratio reached 2·3, the B_4C peaks appeared in XRD pattern along with decreasing TiO_2 to 17·4%wt and increasing TiB_2 to 63·3%wt. It seemed that there was enough amount of B_4C to react with all TiO_2 but maybe the heat treatment time or temperature was not enough to cause consumption of all reactants. At higher ratio of 2·5, an inverse effect appeared and the intensity of TiO_2 peaks increased and the intensity of TiB_2 peaks decreased (figure 5).

Figure 6 shows the effect of B_4C to TTIP molar ratio on weight percent of TiO_2 and TiB_2 at 1100°C. Increasing temperature from 1100°C to 1200°C as the molar ratio is 2·3, resulted in consumption of all reactants and formation of titanium diboride powders. Figures 7 and 8 show the XRD pattern and SEM picture of this sample heated at 1200°C, respectively.

3. Conclusions

Synthesis of titanium diboride powders through a sol–gel method and reduction of hydrolyzed TTIP by boron carbide was studied. Process parameters were optimized to prepare pure TiB_2. When a high concentration TTIP was used, the $Ti(OH)_4$ phase nucleated separately on the B_4C powder surfaces. In the case of low TTIP concentration, required energy for nucleation was not supported, but when the concentration of TTIP was optimum, the mixture of heterogeneous and homogenous nucleation occurred and spherical $Ti(OH)_4$ particles mainly formed on the surface of the B_4C powders. Using molar ratio of B_4C to TTIP less than 2·3 caused the partial consumption of titanium dioxide and consequently having the mixture of TiB_2 and TiO_2 as a main product. Increasing the molar ratio of B_4C to TTIP more than 2·3 resulted in the formation of B_4C–TiB_2 composite powders. The optimum synthesis temperature was 1200°C and pure TiB_2 powders could be prepared using molar composition of $Ti : B_4C = 1 : 2·3$.

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