



# Thermodynamic Prediction and Synthesis of a Titanium Diboride Powder by Reduction of Titanium Dioxide with Boron Carbide in Argon Atmosphere

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## Abstract

An extreme case reaction, the formation of fine titanium diboride (TiB<sub>2</sub>) powder by the reduction of titanium oxide (TiO<sub>2</sub>) with boron carbide (B<sub>4</sub>C) (molar ratio of B<sub>4</sub>C/TiO<sub>2</sub> = 0.714 without carbon black (C)) in the Argon atmosphere, was confirmed through both thermodynamical calculation and experimental results. Because the intermediate product boron-oxide (B<sub>2</sub>O<sub>3</sub>) produced in the extreme case reaction and those of general boro/carbothermal reaction (i.e., molar ratio B<sub>4</sub>C/TiO<sub>2</sub> = 0.5 with 1.5 molar of C) and intermediate reaction (molar ratio of B<sub>4</sub>C/TiO<sub>2</sub> = 0.833 without C) was volatile, excess boron (B) should be added, as in the extreme case reaction, to compensate for the B loss in order to prepare high-purity TiB<sub>2</sub> powder. The experimental results and the reaction mechanism indicate that the formation of TiB<sub>2</sub> powder occurs in the following steps: Firstly, the TiO<sub>2</sub> reduced to titanium carbide (TiC), titanium borate (TiBO<sub>3</sub>), B<sub>2</sub>O<sub>3</sub>, C and TiB<sub>2</sub>. Secondly, the by-product C and B<sub>2</sub>O<sub>3</sub> reacted together to form B<sub>4</sub>C at temperature as high as 1562 °C. Finally, the by-product TiC, TiBO<sub>3</sub> and B<sub>4</sub>C reacted together to complete the TiB<sub>2</sub> formation reaction. The sole suitable situation for obtaining purified fine TiB<sub>2</sub> powder was the extreme case reaction. Experiments indicated that the optimum synthesis temperature and firing time for the extreme case reaction were about 1580 °C and 1 h, respectively. The morphology of the TiB<sub>2</sub> powder that was synthesized resembled a hexagonal shape.

**Keywords** Particle size · Surface area · Titanium diboride · Borocarbide · Hard ceramics

## 1 Introduction

Titanium borides (Ti<sub>2</sub>B, TiB and TiB<sub>2</sub>) are one of the universally explored metal borides due to their various forms. Their amazing properties, such as high chemical stability, outstanding refractory properties and excellent thermal conductivity, have led them to an increased attention in employing for high-temperature applications [1, 2]. In comparison with other forms of titanium boride, titanium diboride (TiB<sub>2</sub>) has gained heightened interest in the industrial sector. This is mainly for its high strength, high stability, durability and erosion resistance [3]. These remarkable characteristics have led titanium diboride to the extensive use in industrial applications, including cutting tools, wear-resistant coatings, electrical

switch interfaces, corrosion resistance and even the extraction of aluminum [2, 4]. Titanium diboride and its composites with ceramics or metals can also be applied as ballistic protection materials [5, 6].

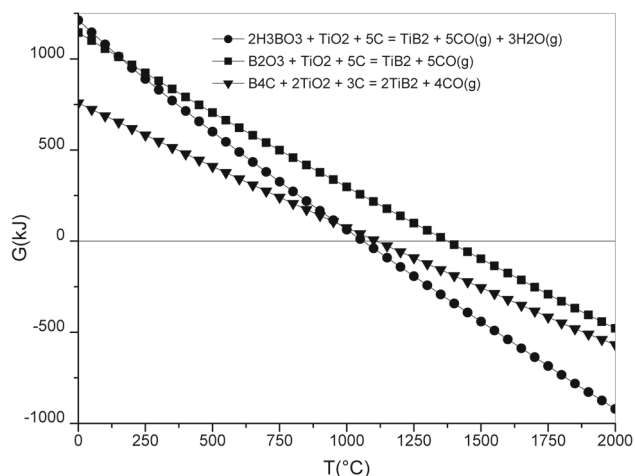
Although the synthesis of metal borides is known for over 100 years, however, their production remains an experimental challenge. Several techniques have been built to prepare titanium diboride powders, including mechanical alloying method, carbothermal reduction technique, sol–gel method self-propagating high-temperature synthesis method, molten salt synthesis and so on [7–15]. From the time of discovery of each technique to produce titanium diboride, chemists, engineers and material scientists have been experimenting to develop inexpensive techniques yielding quality final products with remarkable properties and applications.

Among these conventional techniques the boro/carbothermal and carbothermal reduction processes are the cost-effective techniques to produce metal diboride powders. In these reduction processes the boron carbide (B<sub>4</sub>C), boron trioxide (B<sub>2</sub>O<sub>3</sub>) and boric acid (H<sub>3</sub>BO<sub>3</sub>)

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**Fig. 1** Changes in free energy of formation reactions

are commonly used as boron sources and titanium dioxide ( $\text{TiO}_2$ ) as a titanium source. Beside titanium and boron sources, carbon and boron carbide play the role of a reducing agent. The reduction of titanium dioxide can be illustrated by the following overall reactions:

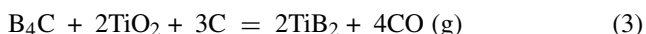
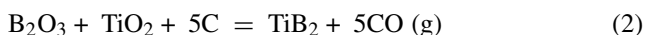
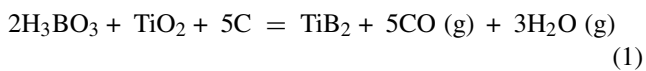
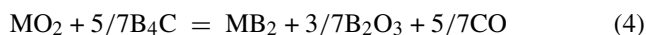


Figure 1 illustrates the changes in the free energy of formation for reactions (1), (2) and (3). It can be estimated from thermodynamic study that the formation of titanium diboride powder from reaction (1) and (3) is possible at temperature as low as 1100 °C (Fig. 1). However, such results have not been reported yet. The titanium diboride powders from boro/carbothermal and carbothermal reduction methods occur almost above 1600 °C. For example, mixtures of titanium dioxide, carbon and boron carbide are reacted at about 1800 °C in an inert atmosphere or vacuum [16]. This means that there are intermediate reactions that occur which divert the pure titanium diboride preparation at a high temperature.

The method in which boron carbide is used as a boron source is the more effective process than others carbothermal reduction process as boron carbide is stable at very high temperatures [17–19] in comparison with others boron sources. Powders prepared through the carbothermal process from boric acid or boron trioxide lead to formation or addition of undesired impurities in the final product as these boron sources can easily volatilize at high temperatures [13, 14, 20].

So far, few researchers have carried out the synthesis of metal diboride such as titanium diboride employing  $\text{TiO}_2$ - $\text{B}_4\text{C}$ -C system [21–23], which is mostly focused on experimental studies to prepare titanium diboride powder with optimum parameters. Currently, there is little available information concerning the thermodynamic analysis of the boro/carbothermal reduction in titanium dioxide-boron carbide-carbon system, but these theoretical data are vital to achieve a titanium diboride powder which predicts the formation mechanism of the deposit. More recently, Yu et al. [21] and Fu and Koc [16] prepared the titanium diboride and titanium diboride-titanium carbide ( $\text{TiC}$ ) powder mixture, respectively, from  $\text{TiO}_2$ - $\text{B}_4\text{C}$ -C mixture. They testified that the boron trioxide intermediate phase formation and its evaporation at high-temperature lead to the deficiency of boron source and thus add impurities to the final products. To avoid this deficiency, they added extra boron carbide contents to get pure titanium diboride. However, this extra boron carbide also added extra carbon to the final product, which was not taken into consideration. In both of these studies, the authors reported the production of boron trioxide by intermediate reaction. However, the reaction path of borothermal reductions to form titanium diboride and boron trioxide has not been discussed. The metal (M) boride such as hafnium diboride ( $\text{HfB}_2$ ) and zirconium diboride ( $\text{ZrB}_2$ ) was also synthesized at relatively low-temperature under vacuum condition using the extreme case boro/carbothermal reduction process as presented by the reaction (4) [24, 25].

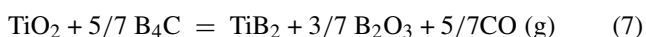
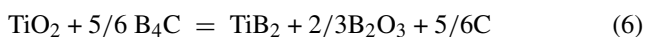
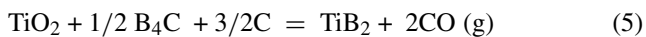


You et al. [26] synthesized tantalum diboride ( $\text{TaB}_2$ ) at 1550 °C in vacuum using the extreme case boro/carbothermal reduction process. Jung et al. [24] synthesized zirconium diboride at 1600 °C in argon atmosphere instead of vacuum using the extreme case boro/carbothermal reduction process. However, these studies were not completely supported by the thermodynamic studies. In this extreme case boro/carbothermal reduction synthesis, which is also termed borocarbide reduction process, the boron carbide is used as both boron and carbon source. The theoretical and experimental analyses on the preparation characteristics of the powder by boro/carbothermal or/and borocarbide reduction process are still a challenge to understand the phenomena involved. To the best of the author's knowledge, the borocarbide reduction synthesis technique has not been reported for titanium diboride preparation in Ar atmosphere with complete thermodynamic studies. Therefore, in the present work, beside the thermodynamic analysis, the synthesis of titanium diboride via borocarbide reduction technique in Ar atmosphere was performed. The influences of different synthesis temperature and different initial reactants composition estimated from general, intermediate and extreme case of

reactions involved in boro/carbothermal reduction process on the titanium diboride formation were discussed to investigate the relevant optimum condition.

## 2 Material and Experimental Techniques

The commercial raw materials, including titanium dioxide (purity  $\geq 99.98\%$ , particle size  $< 10 \mu\text{m}$ ), boron carbide (purity  $\geq 99.0\%$ , particle size  $\leq 10 \mu\text{m}$ ) and carbon black (C, purity  $\geq 99.0\%$ , particle size  $\leq 20 \mu\text{m}$ ) powders, were used as the starting materials. The commercial available  $\text{TiB}_2$  powder (purity  $\geq 99.5\%$ , particle size  $< 20 \mu\text{m}$ ) was used as a standard material. The range of synthesis temperature was predicted from thermodynamic calculation, and the range of firing time was estimated from the reported carbothermal reduction technique [21]. The experiment was carried out under the Ar atmosphere to avoid the oxidation process during synthesis of  $\text{TiB}_2$  powder. The initial raw material estimated from stoichiometric composition of reactions (5) to (7) was well mixed in a mortar-pestle system. Reaction (5) to (7) were designated as general (molar ratio  $\text{B}_4\text{C}/\text{TiO}_2 = 0.5$  with 1.5 molar carbon), intermediate (molar ratio of  $\text{B}_4\text{C}/\text{TiO}_2 = 0.833$  without carbon) and extreme case (molar ratio of  $\text{B}_4\text{C}/\text{TiO}_2 = 0.714$  without carbon) reactions, respectively. Each group of powder mixture was put into the graphite crucible and loaded in a vertical alumina tube (I/D 6 cm) furnace. The sample was heated at  $1580 \text{ }^\circ\text{C}$  for 1 h under the flowing Ar gas with a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . Subsequently, the furnace was cooled down to room temperature by natural rate. The flowing Ar gas was mainly used to avoid the oxidation process during synthesis of  $\text{TiB}_2$  powder. Moreover, the optimal group of a sample was heated at  $1200 \text{ }^\circ\text{C}$  and  $1400 \text{ }^\circ\text{C}$  for 1 h to investigate the reaction mechanism. The whole borocarbide reduction synthesis process was summarized in the form of a flowchart (Fig. 2).



In order to support the optimum group results, the ignition loss of the three groups of synthesized samples at  $1580 \text{ }^\circ\text{C}$  for 1 h was also calculated according to the following formulas:

$$I_r = \frac{M - M_r}{M} \times 100\% \quad (i)$$

$$I_t = \frac{M - M_t}{M} \times 100\% \quad (ii)$$

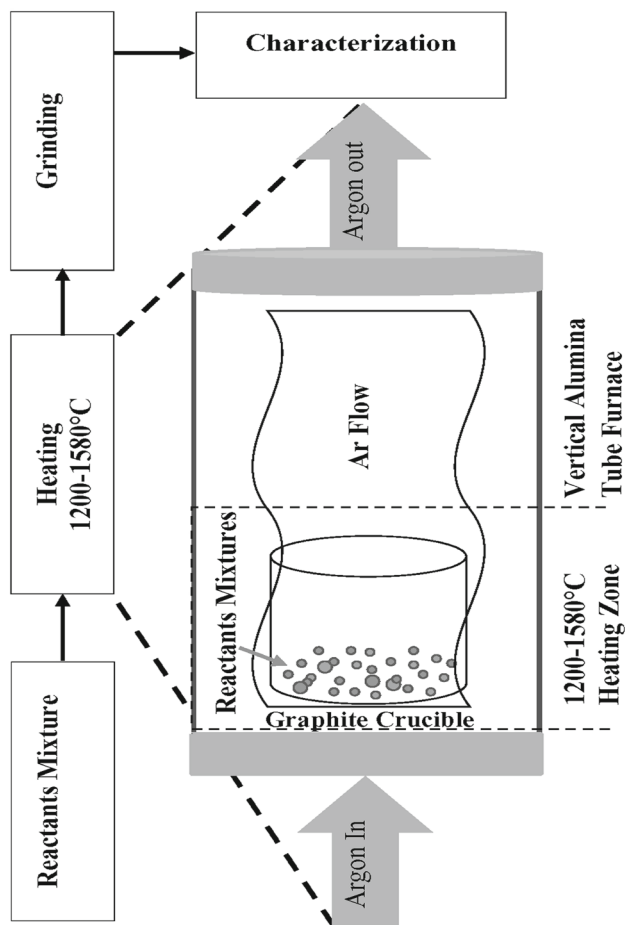


Fig. 2 Flowchart of borocarbide reduction synthesis procedure

where  $I_r$ ,  $I_t$ ,  $M_r$ ,  $M_t$  and  $M$  denote the real ignition loss, theoretical ignition loss, mass of the synthesized products, mass of the desired product according to corresponding reactions (5)–(7) and mass of the total initial reactants, respectively.

The chemical reaction and equilibrium software (HSC chemistry-6) was used to achieve thermodynamic data, including enthalpy and Gibbs free energy value. The qualitative phase analyses of the as-synthesized powders were carried out via X-ray diffraction (XRD) techniques (XRD, PANalytical, XPERTPRO MPD) with  $\text{Cu K}\alpha$  radiation. X-ray diffraction spectra were recorded at 40 mA and 40 kV using  $\text{Cu K}\alpha$  radiation ( $k = 1.5418 \text{ \AA}$ ). For the microstructure observation, the powders were fixed on the alumina stub by an adhesive carbon tape and coated with a thin film of platinum and the micrograph was obtained through a scanning electron microscope (SEM, Semicon, JSM-7001F). The energy-dispersive X-ray spectroscopy (EDS) linked with the scanning electron microscope was used to qualitatively determine the elemental compositions of the synthesized products. The specific surface area was calculated according to the Brunauer, Emmett and Teller (BET) method from  $\text{N}_2$

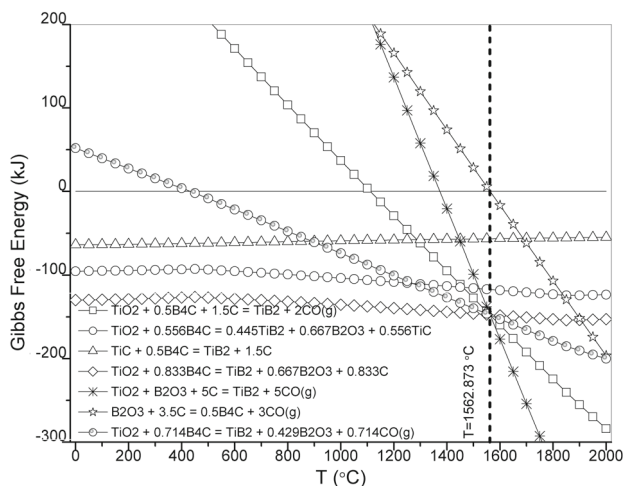


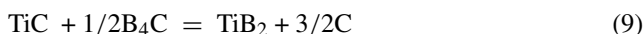
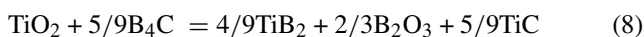
Fig. 3 Relationship between Gibbs free energy and temperature

adsorption–desorption isotherms obtained by AUTOSORB-1 analyzer (Quantachrome).

### 3 Results and Discussion

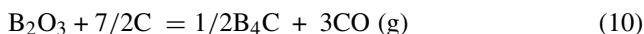
#### 3.1 The Reaction Process

The general reaction (5) is involved in the titanium diboride powders synthesis via boro/carbothermal reduction. However, compliant with the reported results and the current experimental observation, a sublimate boron trioxide phase was observed on the cold flange of the furnace tube at temperatures as low as 1200 °C. It is indicated that the following intermediate reactions may occur at lower synthesis temperature according to the thermodynamic approach (Fig. 3):



The overall reaction (6) can be derived by combining the reactions (8) and (9) with 1:0.833 molar ratios for titanium dioxide and boron carbide.

The high ratio of boron carbide in reaction (6) in comparison with reaction (5) can be acquired at a higher temperature from the carbothermal reaction as follows:



The reaction (10) is the dominant reactions which constraints the completion of the titanium diboride formation reaction via boro/carbothermal reduction technique (i.e., reaction (5)) at low temperature. The general reaction (5) can be deduced by combining the reactions (6) and (10) with

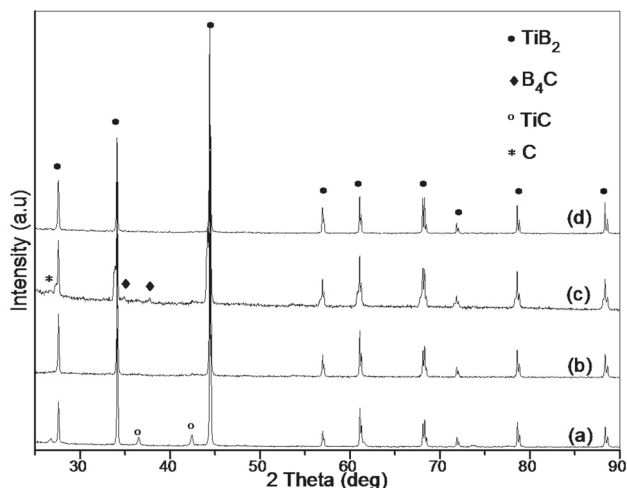
the molar ratio of 1:0.5 for titanium dioxide and boron carbide. In extreme case, the general reaction (5) can be reduced to reaction (7).

In this extreme case reaction (i.e., reaction (7)), the excess of boron carbide generates an extra boron trioxide in the final products according to reaction (8), and the less carbon as an intermediate product (reaction (9)) which is easily consumed to react with the high content of liquid phase intermediated product boron trioxide, according to reaction (10).

The thermodynamic data indicate that the reaction (6) has negative Gibbs energy in the whole synthesis temperature range and thus may occur at every temperature, while the reaction (10) severely occurs at temperature as high as 1562 °C (Fig. 3). The temperature corresponding to the cross-point of the reactions (6) and (10) was at about 1562 °C. The reaction (10) is more significant above the cross-point temperature, while the reaction (6) is important below the cross-point temperature. To investigate the reaction process, in view of present thermodynamic data, the synthesized sample at 1580 °C for 1 h firing time, estimated from the general reactions (5), intermediate reaction (6) and the extreme case general reaction (7) are discussed in the following sections.

#### 3.2 Influence of Different Initial Reactants Composition on Titanium Diboride Powder Formation

The sample, synthesized from the initial reactants of titanium dioxide, boron carbide and carbon estimated from reaction (5) after 1 h firing at 1580 °C, showed the peaks of expected desired phase of titanium diboride along with titanium carbide and carbon (Fig. 4a). The appearance of carbon and titanium carbide peaks indicates that some amount of intermediate product boron trioxide has been evaporated at high temperature, which constraint the completion of intermediate reaction (6). Therefore, the reaction (9) also remained incomplete. Thus, the intermediate product titanium carbide and carbon appeared as impurities. When the initial reactants for the formation of product was estimated from the stoichiometric composition of intermediate reaction (6), the pattern showed the peaks of desired expected phase of titanium diboride along with an unexpected phase of boron carbide (Fig. 4c). The appearance of boron carbide confirmed the reaction mechanism between the intermediate by-product carbon and boron trioxide according to reaction (10). When the initial reactants were estimated from the stoichiometric composition of the extreme case general reaction (7) for the formation of titanium diboride powder, the X-ray diffraction pattern showed the same single phase titanium diboride diffraction pattern as for standard titanium diboride powder sample (Fig. 4b, d). These results confirmed that the reaction (7) is a suitable case for titanium diboride formation from titanium dioxide and boron carbide system at 1580 °C.



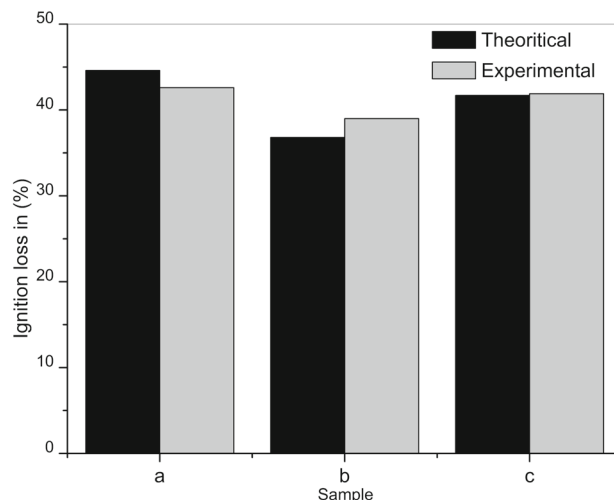
**Fig. 4** X-ray diffraction results of samples, estimated from stoichiometric composition of **a** reaction (5), **b** reaction (7) and **c** reaction (6) fired for 1 h at 1580 °C, **d** standard TiB<sub>2</sub> powder

The comparing between the theoretical and experimental/real loss of ignition could disclose the degree of reaction completion (Fig. 5). In general, if the theoretical ignition loss is smaller than the experimental one, it will indicate low productive rate and high volatilization loss of resultant powders. In the current research work, the experimental ignition-loss of the sample synthesized from the stoichiometric composition of general reaction (5) was 2% smaller than that of the theoretical ignition loss. In sample estimated from intermediate reaction (6), the real loss was 2.2% greater than theoretical value. The experimental ignition loss in the sample synthesized from extreme case general reaction (7) was comparable to the theoretical value, indicating that the titanium diboride formation reaction was completed by reduction of titanium dioxide with boron carbide.

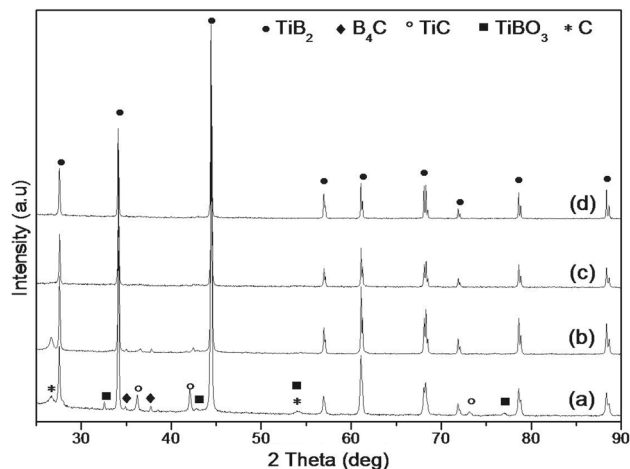
In the reactions (5)–(7), the by-product boron trioxide is a volatile oxide which has the melting temperature and evaporating temperature of 450 °C of 1860 °C, respectively. At high temperature, the boron trioxide loss could occur because of its high vapor-pressure and thus affect the reaction completion. So as to compensate for the loss of boron and to obtain the purified product powder, the excess of boron carbide without using elemental carbon powder in the initial reactant in terms of extreme case of general reaction (i.e., reaction (7)) is the suitable option.

### 3.3 Influence of Synthesis Temperature on the Titanium Diboride Formation

The group of initial reactants estimated from the extreme case general reaction (7) was selected for investigating the different temperatures effect on titanium diboride phase formation (Fig. 6). As shown, titanium diboride was the

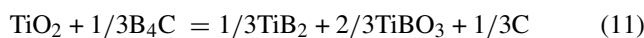


**Fig. 5** Theoretical and experimental ignition losses of the samples estimated from stoichiometric composition of **a** reaction (5), **b** reaction (6) and **c** reaction (7) fired for 1 h at 1580 °C



**Fig. 6** X-ray diffraction results of samples with initial reactants estimated from reaction (7) after firing for 1 h at **a** 1200 °C, **b** 1400 °C, **c** 1580 °C and **d** standard TiB<sub>2</sub> powder

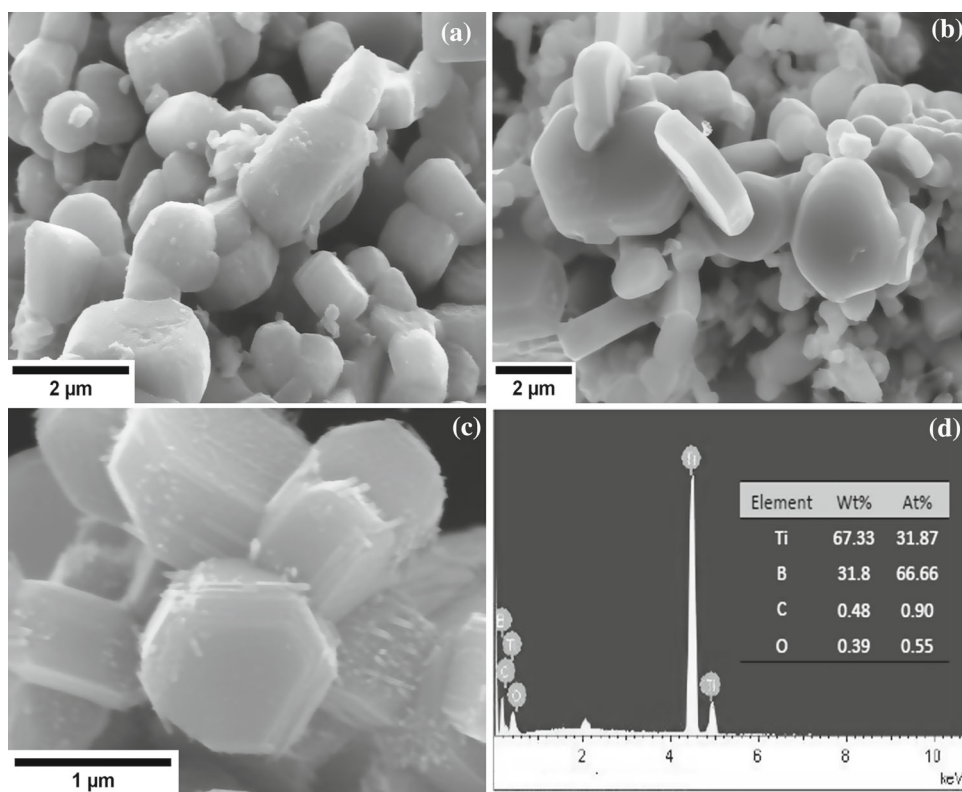
prominent phase at a temperature as low as 1200 °C, whereas the phases of titanium carbide, titanium borate (TiBO<sub>3</sub>) and boron carbide were also found (Fig. 6a). The appearance of titanium borate phase indicates that besides the above-discussed reactions, the following reaction may occur:



The titanium borate phase has also been observed in the previous reports [16, 27, 28]. The titanium borate phase formation may prevent the completion of reactions (8)–(9) at temperature as low as 1200 °C. When the firing temperature was increased to 1400 °C, the titanium carbide and boron carbide phases decreased significantly while the phase of



**Fig. 7** Scanning electron microscope micrograph and qualitative elemental analysis of the sample with stoichiometric composition of reaction (7) after 1 h firing at **a** 1200 °C, **b** 1400 °C, **c** 1580 °C and **d** energy-dispersive X-ray spectroscopy analysis of sample synthesized at 1580 °C



C increased. The phase of titanium borate was almost vanished (Fig. 6b). When the synthesis temperature was further increased to 1580 °C, the unwanted phases of titanium carbide, carbon and the negligible amount of boron carbide were disappeared and the single phase titanium diboride peak was obtained (Fig. 6c). The sample synthesized at 1580 °C showed diffraction pattern as like standard titanium diboride sample (Fig. 6c–d). These results confirmed that the by-product carbon contents as observed in samples synthesized at lower temperature (i.e., 1200 °C and 1400 °C) reacted with the by-product amorphous boron trioxide (expected from reaction (8)) to form boron carbide which next reacted with by-product titanium carbide according to reaction (9) and thus completed the titanium diboride formation reaction.

### 3.4 Microstructural Analysis

The powder synthesized at 1200 °C showed irregular crystal shapes, which could be attributed to inadequate high firing temperature to provide rapid diffusion necessary for the growth of crystallite (Fig. 7a). With increasing temperature to 1400 °C, the hexagonal schistose with inhomogeneous distribution could be intuitively identified owing to the steps forward of reduction reaction (Fig. 7b). Upon further increasing the firing temperature to 1580 °C, the hexagonal shapes with homogenous morphology of titanium diboride crystals

were detected, which could be roughly estimated at less than 2 μm (Fig. 7c). The particle size of the synthesized sample is comparable to the sample synthesized by boro/carbothermal reduction process and smaller than the carbothermal reduction synthesized sample as reported [21, 29–31]

The related energy-dispersive X-ray spectroscopy analysis showed mainly titanium and boron contents, indicating the titanium diboride particle formation (Fig. 7d). The very small quantity of oxygen and carbon were detected by the energy-dispersive X-ray spectroscopy analysis, indicating that the sample is highly pure.

The observed unlabeled peaks were from platinum coating used for scanning electron microscope. The small quantity of carbon content may also belong to carbon tape used for scanning electron microscope instead of by-product material. The free oxygen presence in the sample could originate from the samples handling in non-inert atmospheric laboratory conditions as already reported in the literature [32, 33].

### 3.5 Specific Surface Area

The calculated BET result showed that the  $S_{BET}$  of the fine titanium diboride powders were 5.6 m<sup>2</sup>/g. The  $S_{BET}$  of the studied sample synthesized by borocarbide reduction technique is comparable to the samples synthesized by other conventional methods such as carbothermal and boro/carbothermal reduction techniques [29–31, 34].

## 4 Conclusion

Fine powder of titanium diboride was synthesized by titanium dioxide reduction with boron carbide at 1580 °C. The holding time for synthesis of titanium diboride via borocarbide reduction was 1 h. The synthesized titanium diboride morphology looked like a hexagonal shape. The reaction mechanism indicates that in the first phase, the titanium dioxide reduced to titanium carbide, titanium borate, boron trioxide, carbon and desired product, titanium diboride. In the second phase, the by-product carbon and boron trioxide reacted together to form boron carbide at temperature as high as 1562 °C. Finally, the by-product titanium carbide, titanium borate and boron carbide reacted together to complete the titanium diboride formation reaction. The above results assured that this study provides a new low-temperature synthesis route for nano-sized and micron-sized metal diboride powders.

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## Declarations

**Conflict of interest** The author declares that he has no conflict of interest.

**Data Availability** All data generated or analyzed during this study are included in this article.

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