

Preparation of Titanium Diboride from the Borothermic Reduction of TiO_2 , $\text{TiO}_x(\text{OH})_y$, or $\text{Ti}(\text{O}-n\text{-Bu})_4$ -Derived Polymers

Zhiping Jiang & Wendell E. Rhine

Ceramics Processing Research Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139, USA

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Abstract

The reaction between amorphous boron powder and TiO_2 , $\text{TiO}_x(\text{OH})_y$ or titanium-alkoxide derived polymers ($\text{B}:\text{Ti} = 4:1$) was studied at 25–1500°C in a flow of argon. The borothermic reduction of TiO_2 resulted in formation of Ti_2O_3 and TiBO_3 at 600°C; TiB_2 was formed by further borothermic reduction of Ti_2O_3 and TiBO_3 above 700°C; the overall reaction was found to be complete at 1300°C. The particle sizes of TiB_2 powders obtained were directly related to the starting material used as the titania source. The largest particles were obtained when TiO_2 powder was used as the starting material. The particles were smaller when $\text{TiO}_x(\text{OH})_y$ powder was used, and the smallest particles were obtained when the partially-hydrolyzed Ti polymer, $[\text{BuOTiO}_{1.5}]_n$, was used as the titanium source. The pyrolysis chemistry of these precursors as well as the morphology of the pyrolysis products were studied by FT-IR, TGA, SEM, XRD, BET, elemental analyses and particle size analyses.

Die Reaktion zwischen amorphem Borpulver und TiO_2 , $\text{TiO}_x(\text{OH})_y$ oder von Titanalkoxid abgeleiteten Polymeren ($\text{B}:\text{Ti} = 4:1$) wurde bei 25–1500°C in einem Argonstrom untersucht. Die borothermische Reduktion von TiO_2 führte bei 600°C zur Bildung von Ti_2O_3 und TiBO_3 . Die Bildung von TiB_2 erfolgte bei weiterer borothermischer Reduktion von Ti_2O_3 und TiBO_3 oberhalb von 700°C. Die gesamte Reaktion war bei 1300°C abgeschlossen. Eine Beziehung zwischen erhaltener Teilchengröße der TiB_2 -Pulver und dem Titan-Ausgangsmaterial wurde hergestellt. Die größten Teilchen ergaben sich bei Verwendung von TiO_2 -Pulver als Ausgangsmaterial, während die Teilchen bei Verwendung von $\text{TiO}_x(\text{OH})_y$ kleiner waren. Die kleinsten Teilchen ergaben sich aus

teilhydrolysierten Ti-Polymeren, $[\text{BuOTiO}_{1.5}]_n$. Die Pyrolysechemie der Precursor als auch die Morphologie der Pyrolyseprodukte wurden mit Hilfe von FT-IR, TGA, SEM, XRD, BET, Elementanalyse und Teilchengrößenanalyse untersucht.

Les auteurs ont étudié la réaction entre une poudre de bore amorphe et TiO_2 , $\text{TiO}_x(\text{OH})_y$ ou des polymères dérivés d'alkoxides de titane, et ce entre 25–1500°C dans un flux d'argon. La réduction borothermique conduit à la formation de Ti_2O_3 et TiBO_3 à 600°C; TiB_2 est formé par une réduction borothermique subséquente de Ti_2O_3 et de TiBO_3 au dessus de 700°C; enfin la réaction globale est complète à 1300°C. La taille des particules des poudres de TiB_2 obtenues est directement en rapport avec la matière première utilisée comme source de titane. Les particules les plus grossières correspondent à l'utilisation de TiO_2 , des particules plus fines sont obtenues avec la poudres de $\text{TiO}_x(\text{OH})_y$ et les plus fines lorsqu'on part du polymère de titane partiellement hydrolysé, $[\text{BuOTiO}_{1.5}]_n$. La décomposition pyrolytique et la morphologie des produits de cette polymérisation ont été étudiées par IR à transformée de Fourier, TG, MEB, diffraction RX, BBT, analyse élémentaire et analyse de la distribution granulométrique.

1 Introduction

Titanium diboride (TiB_2) is a hard refractory material, which possesses a high melting point, low electrical resistivity and high thermal conductivity.¹ In addition, sintered TiB_2 is resistant to oxidation to 1100°C and chemically stable in many harsh, corrosive environments.² TiB_2 also has low solubility and is wetted by most molten metals up to

1000°C. The combination of these properties makes TiB₂ a very interesting engineering ceramic material which can be used as ballistic armor, coatings for cutting tools,³ crucibles and electrodes in metal-refining equipment such as aluminium reduction cells.⁴ Furthermore, previous studies indicated that TiB₂ is an excellent component of high-temperature composite materials such as TiB₂/SiC,^{5,6} and TiC/TiB₂.⁷

An important element controlling the commercial success of TiB₂ as an engineered ceramic material is the availability of pure TiB₂ in various forms (powder, whiskers, fibers, etc.) for fabricating materials at low processing temperatures. There are currently four principle methods for preparing TiB₂ powders: synthesis from the elements (Ti and B) at over 2000°C,⁸ reduction of TiO₂ and B₂O₃ by carbon at 2000°C,⁹ reduction of TiO₂ by boron carbide and carbon at 2000°C,^{1,10} and reduction of the titanium and boron halides by hydrogen at 1200°C.¹¹ Except for the latter, these methods require high temperatures. The powders generated from these methods, in general, have large particle sizes (5–30 μm) and require extensive milling before the material can be processed. Titanium diboride powders prepared by carbothermic reduction methods are usually contaminated by carbon and oxygen which adversely affect the mechanical properties of TiB₂.^{1,12} Therefore, improved methods are needed.

In a recent communication¹³ we reported that the reaction between B, C and TiO₂ proceeded by a combination of borothermic and carbothermic reduction reactions. Since the borothermic reduction of TiO₂ proceeded at low temperatures, we decided to examine this approach in more detail. One of the advantages of this method is that the carbon impurity, which usually exists in the TiB₂ products generated from the carbothermic reduction of oxides, can be avoided. However, details about the reaction mechanism, the composition and morphology of intermediate phases for the borothermic reduction of TiO₂, as well as the effect of the Ti source on these factors, are unresolved issues. Our intention was to begin addressing some of these issues of borothermic reduction by reacting boron powder with TiO₂, TiO_x(OH)_y, or Ti(O-*n*-Bu)₄-derived polymer.

2 Experimental Section

TiB₂ was prepared from boron powder and three different titanium oxide sources, TiO₂, TiO_x(OH)_y, and [BuOTiO_{1.5}]_{*n*}. The methods used to prepare the mixtures of boron powder and the Ti source are described below.

2.1 Preparation of mixtures of boron and TiO₂

A mixture of boron powder (Gallery Chemical Company, Gallery, PA, USA) and TiO₂ powder (Fluka AG, Buchs, Germany) in a molar ratio of 4:1 was prepared by adding the powders to a round-bottomed flask and dispersing them in tetrahydrofuran (THF). After the resulting suspension was stirred at room temperature for 2 h, the solvent was removed under vacuum at 100°C, leaving a grayish powder.

2.2 Preparation of mixtures of boron and Ti₂O₃, B₂O₃, or TiBO₃

To study the mechanism for the reaction between boron and TiO₂, mixtures of boron and other oxides were prepared. The same procedure as described above was used to prepare these mixtures of boron with Ti₂O₃, B₂O₃ and TiBO₃. The ratios of oxide to the boron in these samples were Ti₂O₃:7B, 3TiO₂:B, 3TiO₂:B₂O₃:B and TiBO₃:4B.

2.3 Synthesis of TiB₂ precursors from boron and TiO_x(OH)_y

The starting material, TiO_x(OH)_y, for preparation of TiB₂ was synthesized by hydrolyzing titanium butoxide with five equivalents of water (containing ammonium hydroxide) in THF solvent under vigorous stirring. The B:Ti:H₂O ratio of the starting material is 4:1:5; NH₄OH was used as the hydrolysis catalyst. Adding the ammonium hydroxide (NH₄OH) to the Ti(O-*n*-Bu)₄ solution in THF resulted in the immediate formation of a white precipitate. After stirring the suspension for 0.5 h, the boron powder was added into the system. After the resulting dark suspension was stirred for 0.5 h, the volatile components were removed under vacuum at 150°C, leaving a dark powder. This precursor had a nominal composition of 4B/TiO_x(OH)_y (2*x* + *y* = 4).

2.4 Synthesis of TiB₂ precursors from [BuOTiO]_{1.5}

A polymeric titanium precursor was also prepared by partially hydrolyzing titanium butoxide (Ti(O-*n*-Bu)₄) with 1.5 equivalents of H₂O in THF solvent under vigorous stirring. The resulting yellow solution was then mixed with boron powder, yielding a dark suspension (the B:Ti:H₂O ratio in the starting material is 4:1:1.5). After this suspension was stirred at room temperature for 2 h, the volatile components were removed by distillation at 150°C under vacuum, leaving a dark solid, which was insoluble in hydrocarbon solvents. This precursor has a nominal composition of 4B/(BuO)TiO_{1.5}.

2.5 Pyrolysis of precursors

Samples of the above mixtures (0.3–1 g) were placed in carbon crucibles and pyrolyzed in a carbon

furnace under a flow of argon (ultra-high grade) at a flow rate of 300 ml/min. The temperature was increased from room temperature to 1500°C at a heating rate of 200°C/h, held at the desirable temperature for 6 h, and then cooled to room temperature.

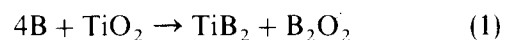
The B₂O₂ by-product was removed by washing the pyrolysis product (0.3 g) in hot water (85°C, 50 ml) for 20 min, and the TiB₂ product was isolated by filtering. The product was dried at 100°C under vacuum.

2.6 Characterization

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies were performed with an infrared (IR) spectrometer (Nicolet PC/IR-44, Nicolet Analytical Instruments, Madison, WI, USA). Samples were prepared by mixing the starting material or the pyrolysis product with dry KBr in a drybox. The ground mixture was transferred into the IR sample cell in the drybox and quickly transferred to the IR spectrometer's sample chamber which was flushed with N₂ for a minimum 10 min before data collection. Thermal decomposition of the starting materials was studied by thermal gravimetric analysis (TGA) (TGA7, The Perkin-Elmer Corporation, Norwalk, CT, USA). X-ray powder diffraction (XRD) patterns were measured with a X-ray diffractometer (Rigaku 300, Rigaku Corporation, Japan) employing CuK α radiation and a Ni filter at a scanning rate of 10°/min. The X-ray peak assignments were carried out using Rigaku software JCPDS peak indexing program. The preparation of the samples for the XRD measurements was performed by grinding the sample in the glove box and putting the resulting fine powder on a piece of greased glass slide to minimize the oxidation and hydrolysis of the samples. When the XRD samples were prepared by grinding the sample in air, dispersing the fine powder in collodion on a glass slide, and drying the slide in an oven, severe hydrolysis and oxidation of boron suboxides were observed. The particle-size distribution (by area) of the pyrolysis products was measured by a centrifugal analysis method (Capa-500, Horiba Inst. Irving, CA, USA) using samples dispersed in isopropanol with an ultrasonic bath. The specific surface area of the product was measured by single-point BET (Quantasorb, Quantachrome Corp., Syosset, NY, USA). The morphologies of the starting materials and the pyrolysis products were observed using a scanning electron microscope (SEM Model S-530; Hitachi Inst. Inc., Mountain View, CA, USA). Elemental analyses were obtained from E + R Microanalytical Laboratory, Inc. (Corona, NY, USA).

3 Results and Discussion

The borothermic reduction of metal oxides is well known,^{9,10,14-17} and Peshev *et al.*¹⁵ have studied the reaction between boron and TiO₂. Based on these previous studies, we expected the borothermic reduction to proceed according to the following reaction:



The B₂O₂ produced by this reaction is reported to be an amorphous solid.¹⁷ To investigate the properties of the titanium diboride obtained by the above reaction, boron was reacted with TiO₂, TiO_x(OH)_y, or partially hydrolyzed titanium butoxide at 500–1500°C. The boron source used in this study was an amorphous powder, which was composed of sub-micrometre particles (the average size of the boron particles dispersed in isopropanol was 0.22 μm based on the centrifugal particle size measurement; the specific surface area was 20.41 m²/g from BET measurements). The elemental analysis of this powder indicated a 94.06% boron content; oxygen was assumed to be the major impurity due to surface oxidation. The TiO₂ sources were crystalline (anatase) TiO₂ powder with an average particle size of 0.63 μm and a specific surface area of 2.94 m²/g, an amorphous titanium hydrous oxide (TiO_x(OH)_y), or the titanium butoxide-derived ([BuOTiO_{1.5}]_n) polymer.

3.1 Synthesis of TiB₂ from boron and TiO₂

Based on the XRD studies, the reaction between TiO₂ and boron powders began at 600°C. The product obtained from TiO₂ and boron powders (B:Ti = 4:1) after heating to 600°C for 6 h was a dark powdery solid. The XRD pattern of the product dispersed in grease indicated that crystalline TiO₂ (anatase), TiBO₃ and Ti₂O₃ were present. After heating the mixture to 700°C, the XRD pattern indicated that the TiO₂ crystalline phase disappeared and TiB₂ appeared (Fig. 1(a)) and was now present in addition to Ti₂O₃ and TiBO₃. Furthermore, the XRD pattern of the product dispersed in collodion (Fig. 1(b)) showed that the same product also contained crystalline B(OH)₃ in addition to TiB₂, Ti₂O₃ and TiBO₃, as indicated by the large diffraction peak at $2\theta = 27.8^\circ$. The small peak at $2\theta = 27.8$ in Fig. 1(a) is due to either TiB₂ or to a small amount of B(OH)₃ that formed during sample preparation. Either the solvents used for or the hydrophilic properties of collodion causes the B₂O₂ in the sample to oxidize and hydrolyze forming B(OH)₃.¹⁷ The oxidation and hydrolysis of B₂O₂ does not occur or is very slow for samples dispersed in a hydrocarbon grease (Fig. 1(a)).

After the mixture of TiO₂ and boron was heated at

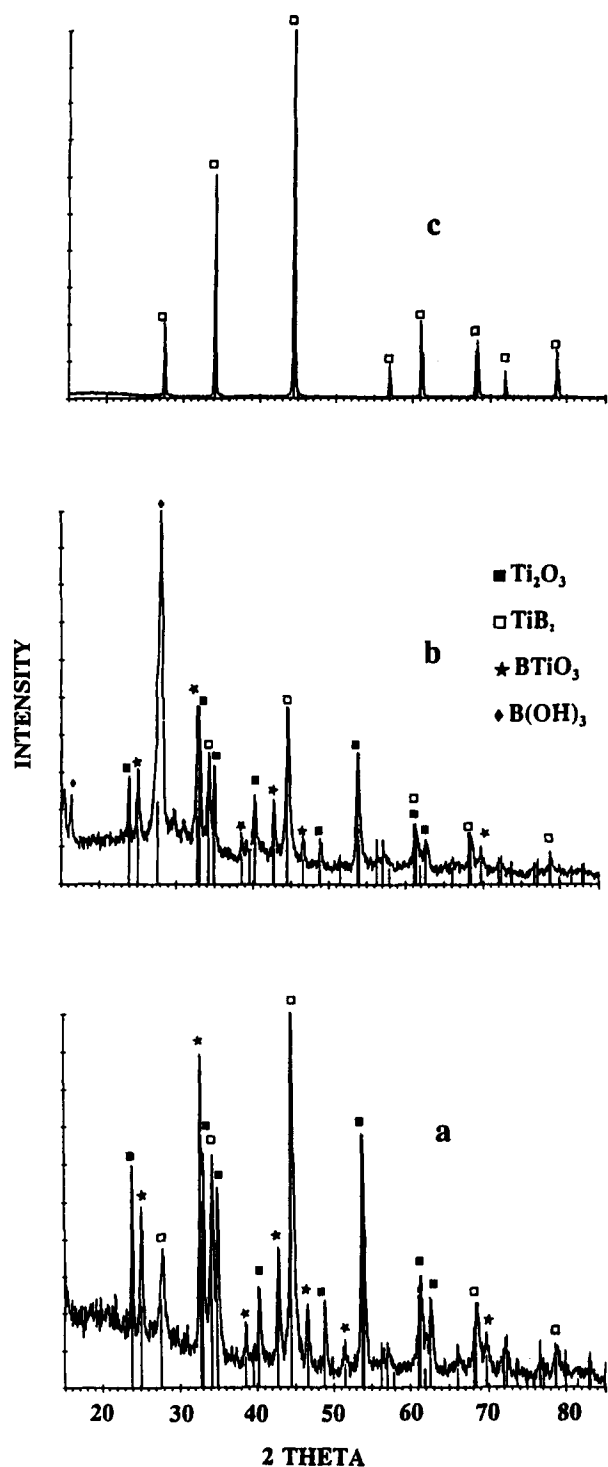


Fig. 1. XRD patterns of the pyrolysis product obtained from a mixture of TiO_2 and boron heated at (a) 700°C, 6 h (in grease), (b) 700°C, 6 h (in collodion), and (c) 1300°C, 6 h (in grease).

Table 1. Pyrolysis residues (wt%) for the mixtures

Ti source	Temperature (°C) ^a			
	700 (6 h)	900 (20 h)	1300 (6 h)	1500 (6 h)
TiO_2	100	100	76.2	51.2
$\text{TiO}_x(\text{OH})_y$	95.1	94.9	76.5	46.1
$[\text{BuOTiO}_{1.5}]_n$	61.1	59.0	32.8	28.3

^a Heating time appears in parentheses.

900°C, the XRD pattern (in grease) of the resulting product indicated that TiB_2 was the only crystalline phase. As indicated in Table 1, no weight loss was observed after firing a mixture of boron and TiO_2 under argon up to 900°C, which indicated that all the B_2O_3 by-product still remained in the product at 900°C. The SEM micrograph of the product heated at 900°C (Fig. 2(a)) indicated that the product contained particles and a glassy phase; the latter phase was presumably B_2O_3 . After this product was washed with hot water to remove the boron oxide, the XRD pattern of the resulting product illustrated that TiB_2 was the only crystalline phase, and the SEM micrograph (Fig. 2(b)) indicated that the product consisted of small agglomerated particles (surface area = 8.57 m²/g).

The elemental analyses of the product heated to 900°C indicated that it contained approximately 10 wt% oxygen, suggesting that the reaction between boron and TiO_2 was not complete at 900°C. Further heating the mixture to 1300°C resulted in a grayish powder. The XRD analysis (in grease) illustrated that TiB_2 was the only crystalline phase (Fig. 1(c)). We determined (Table 1) that a significant weight loss occurred at 1300°C due to the vaporization of boron oxide. However, both SEM and XRD analysis (on collodion) of this product revealed that some boron oxide still remained in the product. The SEM micrograph of the product (Fig. 2(c)) indicated the particle sizes had increased relative to that of the product obtained at 900°C. The average particle size of the product dispersed in isopropanol was 0.74 μm (surface area = 6.65 m²/g). Furthermore, elemental analyses (Table 2) indicated that the product

Table 2. Elemental analyses (wt%) of the products obtained by heating the precursors under argon for 6 h

Ti source	Temperature (°C)	Ti	B	C	H	Ba/Ti
TiO_2	1300 ^a	69.21	30.78	—	—	1.97
	1500 ^b	69.47	30.38	—	—	1.94
$\text{TiO}_x(\text{OH})_y$	1300 ^a	68.34	31.50	0.50	—	2.04
	1500 ^b	68.74	31.38	—	—	2.02
$[\text{BuOTiO}_{1.5}]_n$	1300 ^a	69.17	30.38	0.52	0.55	1.95
	1500 ^b	69.84	30.21	0.35	0.10	1.92

^a After washing with hot water.

^b As-pyrolyzed.

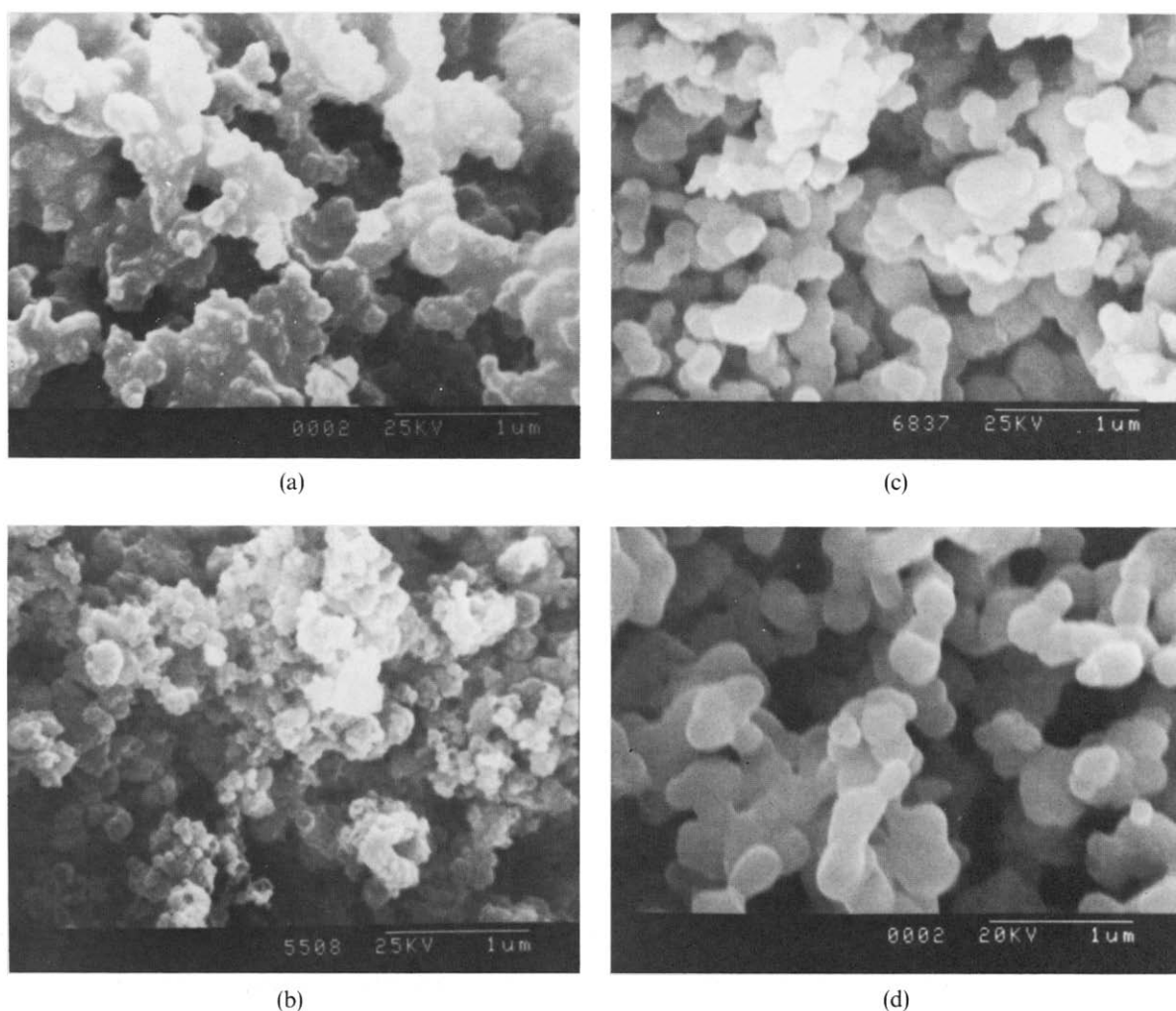


Fig. 2. SEM micrographs of product obtained from a mixture of TiO_2 and boron heated at (a) 900°C for 6 h, (b) the same product as (a) after washing with H_2O , (c) 1300°C for 6 h, after washing, and (d) 1500°C for 6 h, as-synthesized.

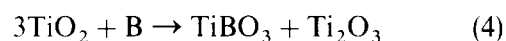
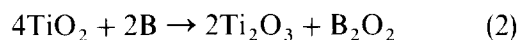
contained a low oxygen content (by difference) and a stoichiometry close to TiB_2 , confirming that the reaction was complete after heating at 1300°C for 6 h.

Heating the mixture to 1500°C resulted in further weight loss (Table 1) due to the vaporization of boron oxide, and the elemental analyses of the as-fired product showed a stoichiometry close to that of the product obtained at 1300°C (after washing). This result suggested that all the boron oxide by-product was vaporized at 1500°C . However, the SEM micrograph (Fig. 2(d)) of this product illustrated that the TiB_2 particles started to coarsen.

Our results were slightly different than Peshev and Bliznakov's.¹⁴ First, in their work, the crystalline TiO_2 (either anatase or rutile) phase remained in the product up to 1500°C ; in addition, they did not observe Ti_2O_3 and TiBO_3 as intermediates. Secondly, our results indicated that the borothermic reduction was complete after heating to 1300°C for 6 h, which was a lower temperature but longer time than that reported in Peshev and Bliznakov's work (1700°C for 1 h).

The presence of Ti_2O_3 and TiBO_3 as intermediate

products suggested that the borothermic reduction of TiO_2 is more complicated than depicted by reaction (1). Based on our XRD results it appears that boron reacts with TiO_2 to form Ti_2O_3 and TiBO_3 , and then these two phases disappear at 900°C , presumably reacting with boron to form TiB_2 . Therefore, we proposed that the following reactions are involved in the borothermic reduction of TiO_2 .



Here, reaction (4) is the combination of reactions (2) and (3).

To confirm reaction (4), a mixture of TiO_2 and boron (3:1 ratio as indicated by reaction 4) was fired at 900°C for 6 h under a flow of argon; Ti_2O_3 and TiBO_3 were the only crystalline phases in the product. Furthermore, since B_2O_2 can be formed from reaction (7),¹⁷ reaction (3) was confirmed by

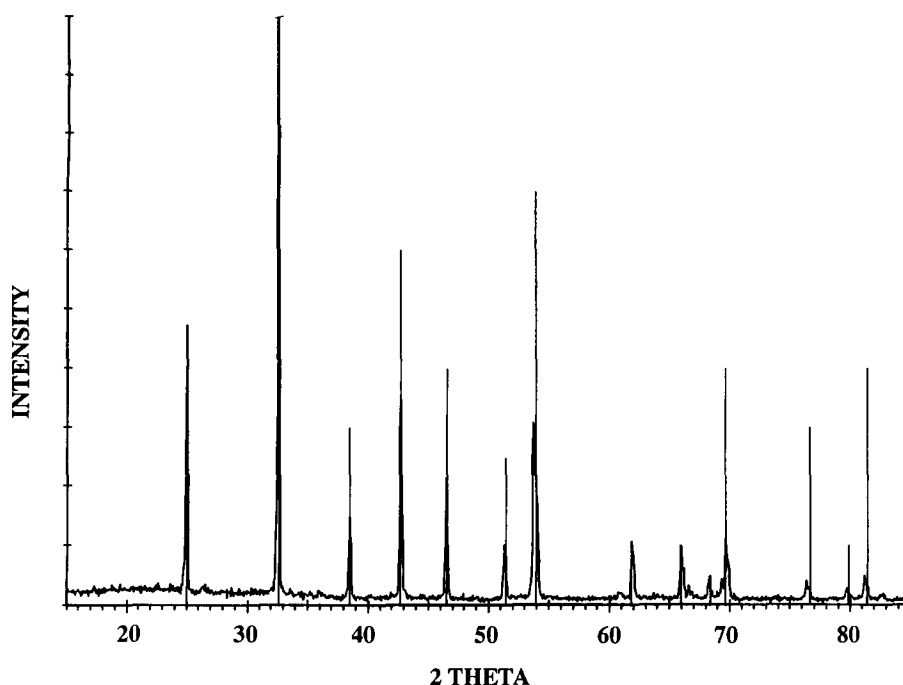
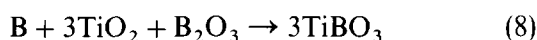
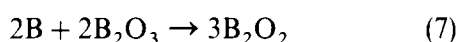


Fig. 3. XRD pattern observed for TiBO_3 .

preparing a sample of TiBO_3 by reaction (8).



Heating a mixture of TiO_2 , B_2O_3 and B in an argon atmosphere for 9.5 h at 700°C resulted in the formation of TiO_2 (rutile) and TiBO_3 . The conversion of anatase to rutile is expected since Pavlikov *et al.*¹⁸ reported that rutile crystallizes from a mixture of B_2O_3 and TiO_2 if heated above 680°C . After heating the mixture at 900°C for 7 h, TiBO_3 was obtained. The product had the same XRD pattern (Fig. 3) as reported by Schmid,¹⁹ and no other phases were observed. Titanium borate was also prepared by reacting B_2O_3 with Ti_2O_3 , but the reaction proceeded slowly and the yield was low. Although TiBO_3 could be prepared by reacting B_2O_3 with Ti_2O_3 , B_2O_3 is not expected to be a product in these reactions. These results imply that reaction (2) proceeds to produce B_2O_2 which subsequently reacts with TiO_2 to produce TiBO_3 as indicated by reaction (3).

Reaction (5) was confirmed by heating a mixture of boron and Ti_2O_3 (7B: Ti_2O_3) in an argon atmosphere at 900°C for 20 h; the XRD pattern of the resulting product indicated that TiB_2 was the major phase present and a small amount of unreacted Ti_2O_3 still remained. Reaction (6) was confirmed by heating a mixture of TiBO_3 and B at 900°C for 13 h, and TiB_2 was the only product obtained.

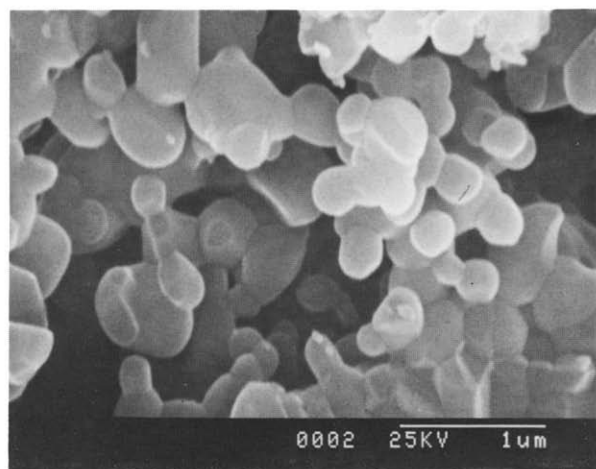
3.2 Synthesis of TiB_2 from boron and $\text{TiO}_x(\text{OH})_y$

The TiB_2 particles obtained from the mixture of boron and $\text{TiO}_x(\text{OH})_y$ powders were similar to those

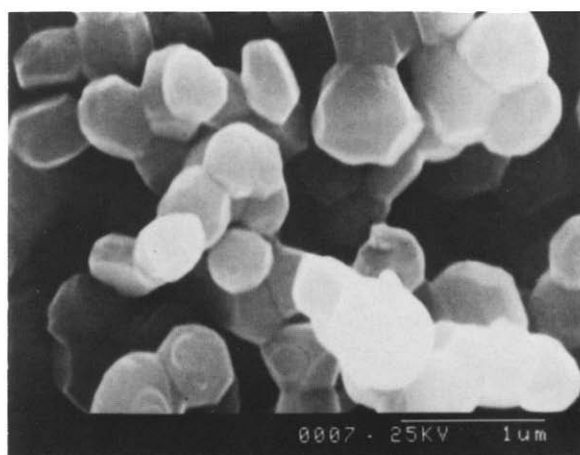
obtained from the mixture of TiO_2 and boron, but there was a significant difference in the particle sizes obtained. Pyrolyzing this mixture in an argon atmosphere at 900°C for 6 h resulted in small particles of TiB_2 (surface area = $20.34 \text{ m}^2/\text{g}$). After heating at 1300°C for 6 h, the small particles of TiB_2 increased in size (Fig. 4(a)) ($0.2\text{--}0.7 \mu\text{m}$; surface area = $8.11 \text{ m}^2/\text{g}$), and heating the mixture to 1500°C increased the particle sizes further (Fig. 4(b)). Although the product obtained at 900°C had a high surface area, SEM micrographs of the products obtained at 1300 and 1500°C indicated that the individual particles were larger than those obtained from TiO_2 . A small weight loss was observed for the mixture at $700\text{--}900^\circ\text{C}$ (Table 1); the weight loss below 900°C for the mixture of $\text{TiO}_x(\text{OH})_y$ and boron was attributed to the condensation of Ti-OH groups and subsequent evolution of H_2O . In addition, the elemental analyses (Table 2) of products at 1300 and 1500°C indicated a B/Ti ratio of 2.02 and low carbon contents.

3.3 Synthesis of TiB_2 from boron and $\text{Ti}(\text{O}-n\text{-Bu})_4$ derived polymers

The mixture of boron and $[\text{BuOTiO}_{1.5}]_n$ was synthesized by partially hydrolyzing the Ti butoxide and mixing the resulting Ti polymer with boron powder. The FT-IR spectrum of the as-synthesized mixture of boron and $[\text{BuOTiO}_{1.5}]_n$ (Fig. 5(a)) is similar to the spectrum reported previously²⁰ and indicated the existence of the $-\text{OBu}$ groups; they are represented by the strong C-H stretching (2960 , 2929 and 2870 cm^{-1}) and C-H bending (1461 and 1375 cm^{-1}) vibrations. In addition, the broad band below 900 cm^{-1} in the IR spectrum is attributed to



(a)



(b)

Fig. 4. SEM micrographs of the product obtained from a mixture of $\text{TiO}_x(\text{OH})_y$ and boron (a) heated at 1300°C for 6 h, after washing, and (b) heated at 1500°C for 6 h, as-synthesized.

the polymeric Ti–O units in the precursor. The broad absorption band around 3300 cm^{-1} is assigned as the Ti–O–H stretching vibration; these OH groups could be due to the hydrolysis of Ti–O–Bu units during the IR measurement.

Pyrolysis of this mixture of boron and $[\text{BuOTiO}_{1.5}]_n$ in argon resulted in the decomposition of –O–Bu groups and condensation of Ti–OH groups. By 300°C , no organics were left in the product based on the IR spectra (Fig. 5(b)). Table 1 lists the weight of the pyrolysis residues obtained between 700 and 1500°C and reveals that there is almost a 40% weight loss by 700°C . The XRD pattern of the 600°C as-pyrolyzed product dispersed in grease indicated that TiBO_3 was the only crystalline phase; at 700°C , TiB_2 was observed in addition to TiBO_3 . Heating the precursor to 900°C increased the crystallinity of TiB_2 , and the XRD peaks corresponding to TiBO_3 disappeared. We noticed, based on the XRD results, that no crystalline titanium oxides formed during the pyrolysis between 600 and 900°C , which indicates that any reduced titanium oxides are present in the amorphous state.

After the product obtained at 900°C was washed with hot water, the resulting product consisted of large ($30\text{--}100\ \mu\text{m}$), irregularly shaped agglomerates which could easily be milled into fine particles. An SEM micrograph (Fig. 6(a)) revealed that these agglomerates were loosely connected and consisted of fine particles. BET studies indicated that this product possessed a specific surface area of $24.23\text{ m}^2/\text{g}$, which is three times higher than that ($8.57\text{ m}^2/\text{g}$) for the product obtained from TiO_2 powder under the same conditions. The calculated

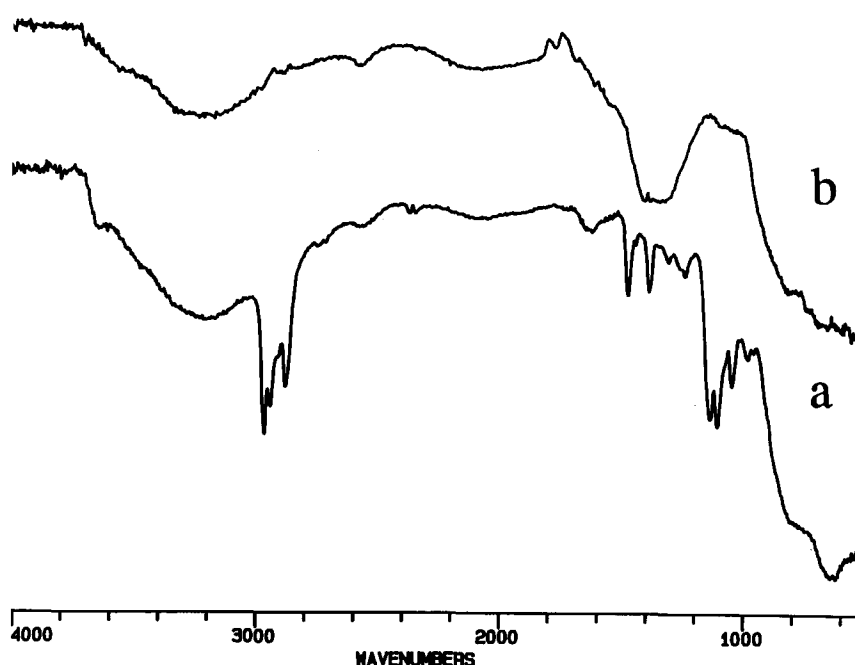
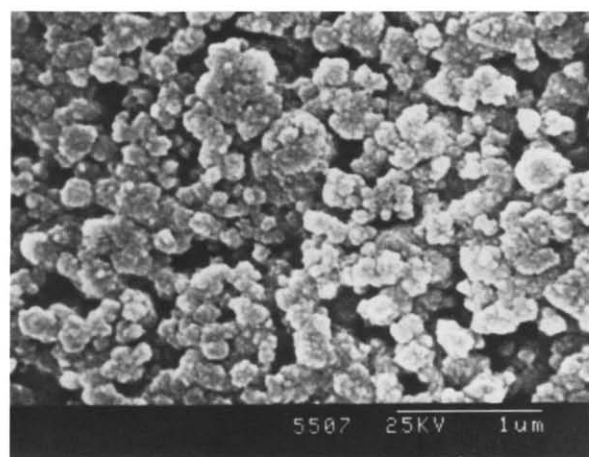
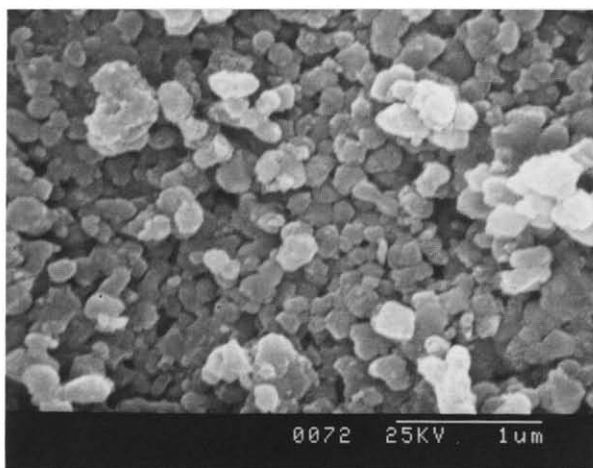


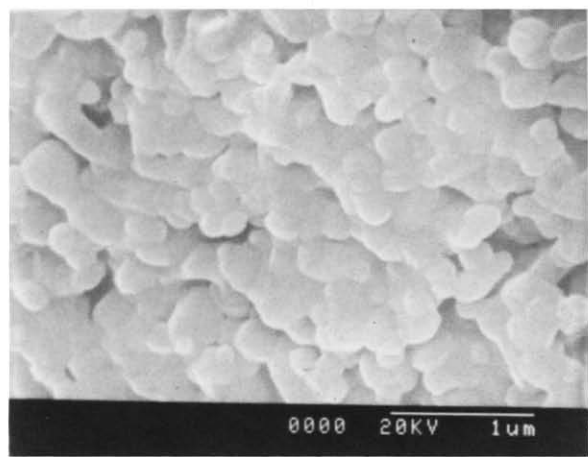
Fig. 5. IR spectra of the mixture of boron and $[\text{BuOTiO}_{1.5}]_n$: (a) as prepared and (b) after heating to 300°C .



(a)



(b)



(c)

Fig. 6. SEM micrographs of the product obtained from a mixture of $[\text{BuOTiO}_{1.5}]_n$ and boron: (a) heated at 900°C for 6 h, after washing, (b) heated at 1300°C for 6 h, after washing, and (c) heated at 1500°C for 6 h, as-synthesized.

equivalent spherical particle size for the TiB_2 powders were 0.055 and $0.156\ \mu\text{m}$, respectively.

The differences in particle sizes and surface areas between the products generated from the mixture of boron and TiO_2 and the mixture of boron and $[\text{BuOTiO}_{1.5}]_n$ could arise because the latter method provides more intimate mixing between reactants

Table 3. Surface areas (m^2/g) for pyrolysis residues

Ti source	Temperature ($^\circ\text{C}$) ^a		
	900	1300	1500
TiO_2	8.57	6.65	—
$\text{TiO}_x(\text{OH})_y$	20.34	8.11	—
$[\text{BuOTiO}_{1.5}]_n$	23.42	18.99	1.27

^aHeated for 6 h under argon.

than does mixing boron and TiO_2 powders. Therefore, upon decomposition and subsequent borothermic reduction, the mixture of boron and partially hydrolyzed titanium butoxide, $[\text{BuOTiO}_{1.5}]_n$, yielded smaller particles and a highly agglomerated structure.

It is also possible that the observed particle size differences are related to the particle size of the Ti source material. When boron and $\text{TiO}_x(\text{OH})_y$ powders were mixed, the surface area of the product obtained at 900°C was also high ($20.34\ \text{m}^2/\text{g}$). The surface areas for the products are summarized in Table 3. The particle sizes of the TiB_2 product obtained are directly proportional to the expected particle size of the titania source material ($\text{TiO}_2 > \text{TiO}_x(\text{OH})_y > \text{pyrolyzed } [\text{BuOTiO}_{1.5}]_n$). More research would be needed to determine whether the particle size of the titania source or the level of mixing is more important.

After the mixture of boron and $[\text{BuOTiO}_{1.5}]_n$ was heated at 1300°C for 6 h, the XRD pattern (on collodion) indicated sharp TiB_2 peaks, and the elemental analyses of this product revealed that the borothermic reduction was complete. An SEM micrograph (Fig. 6(b)) illustrated that the TiB_2 particles coarsened slightly, but the surface area determination indicated that the surface area decreased only slightly ($18.99\ \text{m}^2/\text{g}$). Further heating the precursor to 1500°C removed the remaining B_2O_2 by-product. SEM micrographs indicated that the particles have increased in size and appear partially sintered (Fig. 6(c)). The surface area decreased to $1.27\ \text{m}^2/\text{g}$ after heating at 1500°C for 6 h.

In summary, TiB_2 powders with submicron sizes can be prepared by the borothermic reduction of TiO_2 or $\text{TiO}_x(\text{OH})_y$ powders or $[\text{BuOTiO}_{1.5}]_n$ at 1300°C for 6 h. The borothermic reduction of TiO_2 began with the formation of Ti_2O_3 and TiBO_3 which subsequently reacted with boron to form TiB_2 . The particle size and mixing of the precursors had an effect on the particle size of the TiB_2 products, and the surface area of the TiB_2 product appeared to depend on the titanium starting material. As the mixing between boron and titanium became more intimate, the surface area of the product (at any given temperature) increased. For example, when the

partially-hydrolyzed Ti butoxide-derived polymer was used as the Ti source, very small TiB₂ particles were obtained, and at 1500°C the particles appeared to be partially sintered.

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References

- Kim, J. J. & McMurtry, C. H., TiB₂ powder production for engineered ceramics. *Ceram. Engng Sci. Proc.*, **6**(9–10)(1985) 1313–20.
- Greenwood, N. N., *Comprehensive Inorganic Chemistry* (Vol. 1), ed. J. C. Bailar Jr, H. J. Emeleus, R. Nyholm & A. F. Trotman-Dickenson. Pergamon Press, Oxford, UK, 1973, p. 697.
- Funk, R., Lux, B., Schachner, H. & Tannenberger, H., Increasing the wear resistance of surface hard metal part. (French Patent 2144823, 1973.) *Chem. Abstr.*, **79** (1973) 107206.
- Murata, Y. & Miccioli, B. R., Inhibition of grain growth in niobium diboride. *Am. Ceram. Soc. Bull.*, **50** (1971) 182–5.
- Janney, M. A., Mechanical properties and oxidation behavior of a hot-pressed SiC 15 vol% TiB₂ composite. *Am. Ceram. Soc. Bull.*, **66**(2) (1987) 322–4.
- McMurtry, C. H., Boecker, W. D. G., Seshadri, S. G., Zanghi, J. S. & Garnier, J. E., Microstructure and material properties of SiC–TiB₂ particulate composite. *Am. Ceram. Soc. Bull.*, **66**(2) (1987) 325–9.
- Watanabe, T., Effects of carbide addition on the mechanical properties of the Ti(C_{0.5}, N_{0.5})-30 wt% TiB₂-carbide sintered compacts. *J. Ceram. Soc. Japan*, **99**(2)(1991) 146–9.
- Palty, A. E., Margolin, H. & Nielsen, J. P., Titanium–nitrogen and titanium–boron systems. *Trans. Am. Soc. Metals*, **46** (1954) 312–28.
- Thompson, R., *Progress in Boron Chemistry* (Vol. 2), Pergamon Press, New York, USA, 1975, p. 195.
- Greenwood, N. N., Parish, R. V. & Thornton, P., *Quart. Rev.*, **20** (1966) 444–5.
- Gannon, R. E., Folweiler, R. C. & Vasilos, T., Pyrolytic synthesis of titanium diboride. *J. Am. Ceram. Soc.*, **46**(10) (1963) 496–9.
- Walker, J. K., Synthesis of TiB₂ by borothermic/carbothermic reduction of TiO₂ with B₄C. *Adv. Ceram. Mater.*, **3**(6) (1988) 601–4.
- Jiang, Z. & Rhine, W. E., Preparation of titanium diboride from titanium alkoxide and boron powder. *Chem. Mater.*, **4** (1992) 497.
- Peshev, P. & Bliznakov, G., On the borothermic preparation of titanium alkoxide and boron powder. *J. Less-Common Metals*, **14** (1968) 23–32.
- Peshev, P., Leyarovska, L. & Bliznakov, G., On the borothermic preparation of vanadium, niobium, and tantalum borides. *J. Less-Common Metals*, **15** (1968) 259–67.
- Peshev, P., Bliznakov, G. & Leyarovska, L., On the preparation of some chromium, molybdenum, and tungsten borides. *J. Less-Common Metals*, **13** (1967) 241–7.
- Barton, L. & Nicholls, D., The hydrogenation of monoxide to diboride and the reaction of boron and boron carbide with titanium and zirconium diboride. *J. Inorg. Nucl. Chem.*, **28** (1966) 1367–72.
- Pavlikov, V. N., Yurchenko, V. A. & Tresvyatskii, S. G., The B₂O₃–TiO₂ system. *Zh. Neorg. Khim.*, **21** (1976) 233; *Russ. J. Inorg. Chem.*, **21** (1976) 126.
- Schmid, H., X-ray evidence for CrBO₃, VBO₃, and TiBO₃ with calcite structure. *Acta Cryst.*, **17** (1964) 1080.
- Jiang, Z. & Rhine, W. E., Preparation of TiN and TiC from a polymeric precursor. *Chem. Mater.*, **3** (1991) 1132.