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Synthesis of ultrafine titanium diboride particles by rapid carbothermal reduction in a particulate transport reactor

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Ultrafine TiB_2 powders were synthesized by rapid carbothermal reduction in a vertical tubular reactor through which the particles fell freely. The starting materials were TiO_2, H_3BO_3 and cornstarch, which were mixed and calcined at 400 °C for 1 h. The calcined precursor was milled, sieved and then fed into the top of the reactor. The reduction was carried out between 1786–1791 °C in a downward flow of argon. Product particles were recovered at the bottom of the reactor. When the precursor molar composition ratio was $TiO_2 : B_2O_3 : C = 1 : 2 : 5.5$, the carbon content in the product was 5 wt % and the crystallite size was 80 nm. The carbon content in the product was reduced to 2.9 wt % by a heat treatment in an H_2 atmosphere for 9 h.

1. Introduction

Titanium diboride (TiB_2) possesses superior thermal, mechanical and chemical properties and, as a result, has broad applications in cutting tools, wear parts and jet engine components [1]. Normally, TiB_2 is produced by reducing titanium oxide with either (1) boron oxide and carbon, (2) boron and carbon, (3) boron carbide or (4) an alkali metal and boron oxide. These processes typically require long reaction periods, during which the TiB_2 particles are sintered. A subsequent size-reduction step results in product contamination. Doi [2] has reported that the impurity content in TiB_2 powders was approximately 35 wt % after a size reduction from 7 to 1 μm in a WC–Co alloy ball mill. Nishiyama [3] has reported that the impurity content in TiB_2 powders was approximately 20 wt % when the average particle size was decreased from 6 to 2.5 μm by a 3 h ball milling in a WC/Co pot with WC/Co balls.

Since single-component TiB_2 particles are difficult to sinter, additives such as Cr/C, Al_2O_3, ZrO_2, Ni/C, SiC and yttria stabilized zirconia (YSZ) are applied in order to increase the density [4–8]. Baumgartner and Steiger [9] sintered a TiB_2 powder with a 0.1–1 μm, particle size produced by an arc-plasma method from $TiCl_4$ and BCl_3 in H_2, and achieved a relative density higher than 98% by pressureless sintering at 2000 °C. Densification proceeded by self diffusion due to a high grain-boundary area. Thus, it is essential to establish processes which produce TiB_2 particles whose size is in the range of tens of nanometers.

Recently the group of Weimer [10–12] succeeded in producing B_4C particles containing a small amount of TiB_2 particles via rapid carbothermal reduction. The overall reactions of the carbothermal reduction are expressed as follows:

$$2B_2O_3(l) + 7C(s) \rightarrow B_4C(s) + 6CO(g) \quad (1)$$

$$TiO_2(s) + B_2O_3(l) + 5C(s) \rightarrow TiB_2(s) + 5CO(g) \quad (2)$$

The starting materials, TiO_2, H_3BO_3 and cornstarch, with TiO_2 and carbon as the limiting components, were calcined at 400 °C in a N_2 atmosphere. After pulverization, the precursor particles with a particle size less than 44 μm were fed into a vertical tubular reactor by a screw feeder. Dispersion of the precursor particles in the gas phase and a short residence time in the reactor prevented the particles from sintering.

Stanley *et al.* [13] used titanium isopropoxide as the metal source, boron triethoxide as the boron source and furfuryl alcohol as the carbon source. The precursor particles contained TiO_2 particles of 50–100 nm in size that were reduced to TiB_2 in a horizontal tubular reactor. They obtained 1–3 μm sized TiB_2 particles in the shape of well-defined hexagonal platelets and claimed that the intimate mixture of reactants in the precursor decreased the carbon content in the product. Maeda *et al.* [14] synthesized NbB_2 powders by rapid carbothermal reduction with a precursor prepared from Nb_2O_5, H_3BO_3 and cornstarch in a vertical particulate transport reactor. They concluded that the rate-determining step was NbB_2 formation from

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TABLE I Reactions of rapid carbothermal reduction

Products	Overall reaction scheme	Temperature	Major reaction	Reaction type
$\beta - SiC$[15]	$3C(s) + SiO_2(s) \rightarrow SiC(s) + 2CO(g)$	1600–2000 °C	$C(s) + SiO_2(s) \rightarrow SiO(g) + CO(g)$ $2C(s) + SiO(g) \rightarrow SiC(s) + CO(g)$	Gas–solid
B_4C[10–12]	$7C(s) + 2B_2O_3(l, g) \rightarrow B_4C(s) + 6CO(g)$	1500–1850 °C	$C(s) + B_2O_3(l, g) \rightarrow B_2O_2(g) + CO(g)$ $7C(s) + 2B_2O_3(l) \rightarrow B_4C(s) + 4CO(g)$ $5C(s) + 2B_2O_2(g) \rightarrow B_4C(s) + 4CO(g)$	Liquid–solid (Gas–solid)
NbB_2 [14]	$Nb_2O_5(s) + 2B_2O_3(l) + 11C(s) \rightarrow 2NbB_2(s) + 11CO(g)$	1500–1800 °C	$C(s) + B_2O_3(l, g) \rightarrow B_2O_2(g) + CO(g)$ $Nb_2O_5(s) + 7C(s) \rightarrow 2NbC(s) + 5CO(g)$ $NbC(s) + B_2O_3(l, g) + 2C(s) \rightarrow NbB_2(s) + 3CO(g)$ $NbC(s) + B_2O_2(g) + C(s) \rightarrow NbB_2(s) + 3CO(g)$	Liquid–solid–solid (Gas–solid–solid)
AlN [16]	$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g)$	1400–1850 °C	$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g)$	Gas–solid–solid
SiN [17, 18]	$6C(s) + 3SiO_2(s) + 2N_2(g) \rightarrow Si_3N_4(s) + 6CO(g)$	1350–1550 °C	$C(s) + SiO_2(s) \rightarrow SiO(g) + CO(g)$ $3C(s) + 3SiO(g) + 2N_2(g) \rightarrow Si_3N_4(s) + 3CO(g)$	Gas–gas–solid
TiN [19–21]	$2TiO_2(s) + 4C(s) + N_2(g) \rightarrow 2TiN(s) + 4CO(g)$	1100–1250 °C	$6TiO_2(s) + 3C(s) \rightarrow 2Ti_3O_5(s) + 2CO(g) + C(s)$ $2Ti_3O_5(s) + 10C(s) + 3N_2(g) \rightarrow 6TiN(s) + 10CO(g)$	Gas–solid–solid

NbC, B_2O_3 and C. The initial particle size of the Nb_2O_5 starting material was an important factor in achieving a high conversion, whilst the calcination temperature controlled the residual carbon content in the products. The reaction temperature affected the crystal size of the products. By optimizing the experimental conditions, NbB_2 particles 40–50 nm in size were synthesized with a carbon content of 2.65 wt %. The products and rapid carbothermal reduction schemes are summarized in Table I.

The present study describes the production of submicrometre sized TiB_2 particles via rapid carbothermal reduction, using precursors prepared from TiO_2, H_3BO_3 and cornstarch. The carbon content in the product is decreased by a heat treatment in a hydrogen atmosphere.

2. Experimental procedure

2.1. Precursor synthesis

Fig. 1 shows the TiO_2 particles (supplied by Ishihara Sangyo Co.) used as the titanium source. The average size was 40–50 nm as measured by field-emission scanning electron microscopy (SEM, Hitachi S-900) and approximately 30 nm by X-ray diffraction (XRD, Shimadzu XD-D1). The latter was calculated from the width of the main TiO_2 (110) peak. Reagent grade TiO_2, H_3BO_3 and cornstarch (Wako Pure Chemical) were mixed at prescribed ratios in deionized water at ambient temperature, and the mixture was evaporated by boiling with stirring. After the mixture became viscous, it was placed in an oven at 95 °C and dried overnight. The white flakes obtained were calcined at 400 °C for 60 min in an argon atmosphere. Thus, the starting materials were converted to a mixture of TiO_2, B_2O_3 and carbonaceous matter. The calcined black flakes were pulverized in a ball mill for 4–12 h. The carbon content in the precursor was determined by elementary analysis after removal of the B_2O_3 by washing with methanol. The boron oxides in the precursors and products were dissolved in methanol, and the boron concentration was evaluated by inductively coupled plasma spectrometry (Seiko, SPS 1200VR).

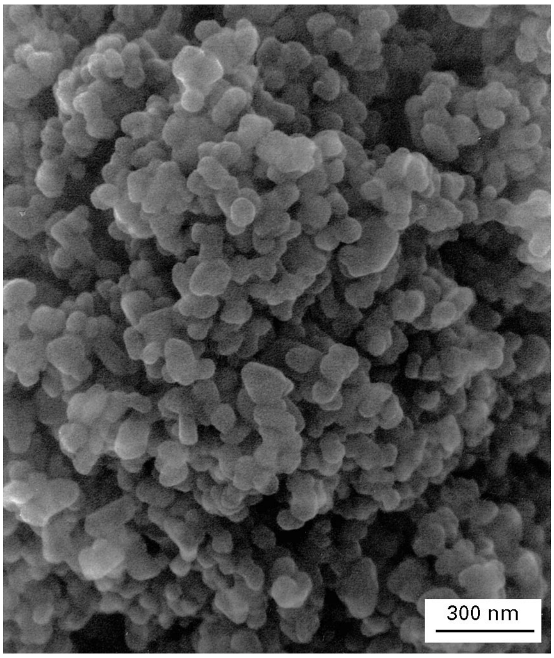

Figure 1 Morphology of the TiO_2 particles.

2.2. Carbothermal reduction

Fig. 2 shows the continuously operated reactor used for the rapid carbothermal reduction. The outer

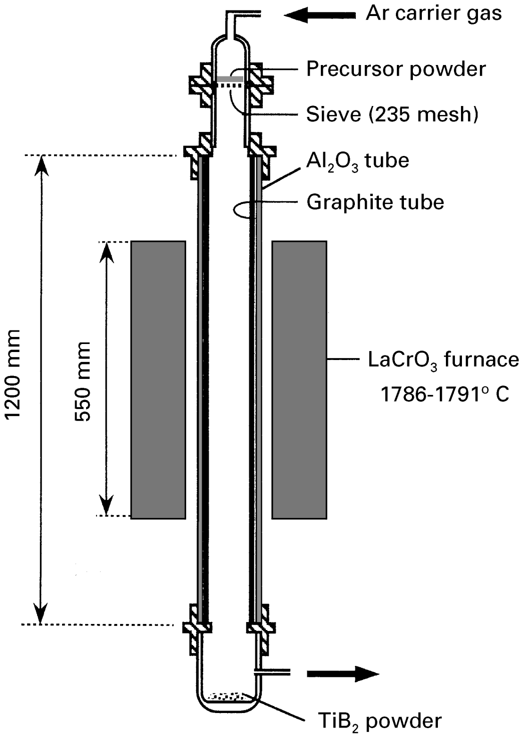

Figure 2 The particulate transport reactor used for the rapid carbothermal reduction.

column was a 1.2 m long alumina tube having a 36 mm internal diameter. The inner one was a 19 mm internal diameter graphite pipe which was used to protect the alumina tube from any reaction with the boron oxides. The pulverized precursor powder was stored in a 235 mesh metal sieve on top of the reactor and was introduced into the reactor through the mesh by manual tapping. The reactor was heated by $LaCrO_3$ heaters, and the isotherm zone of 1786–1791 °C was approximately 4–5 cm in length. The product was collected in a flask fixed at the cooled bottom of the reactor. The reaction was always carried out in an Ar atmosphere at ambient pressure. The average velocity of the Ar carrier gas was 4 cm s^{-1} at 1791 °C. Since the free fall velocity of the precursor particles of 30 μm diameter was approximately 1 cm s^{-1}, the residence time in the isotherm zone was approximately 1 s. To decrease the carbon content the particles of the product were treated in a H_2 atmosphere at 800 °C for 3–18 h. The reaction rate was also determined using a horizontal tubular reactor of 1 cm diameter. The precursor was placed in a molybdenum boat and was maintained at a temperature of 1350–1500 °C for a prescribed period. The sample was then analysed by XRD.

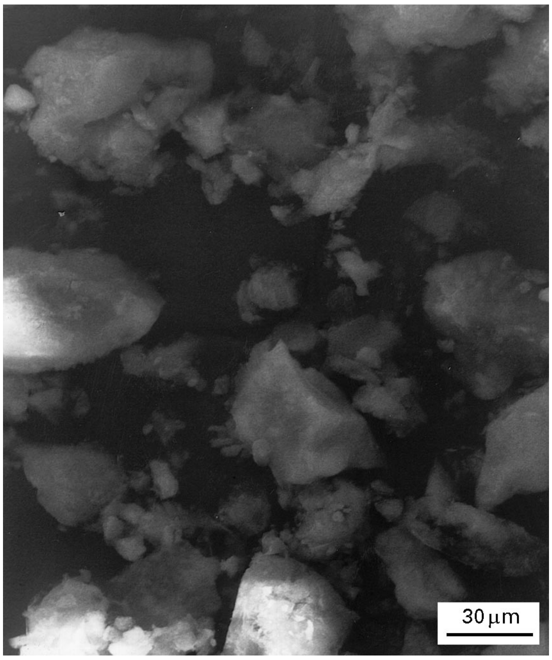

Figure 3 Morphology of the precursor particles.

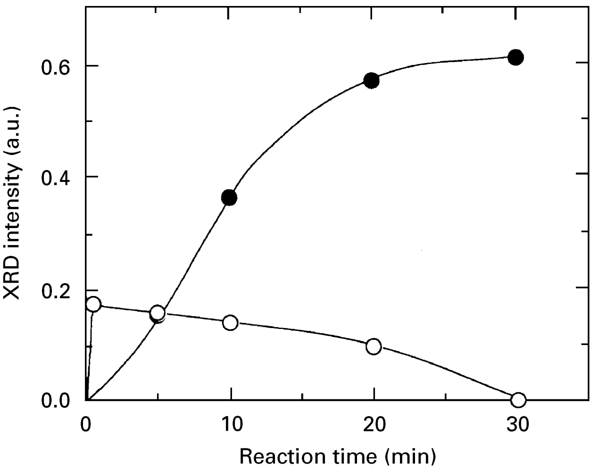

Figure 4 Formation of: (○) TiC and (●) TiB_2 in a horizontal tubular reactor at 1350 °C.

3. Results and discussion
3.1. Effects of reaction conditions on product particles

Fig. 3 shows the morphology of the precursor particles after calcination at 400 °C for 1 h. The precursor was prepared at a molar composition of $TiO_2 : B_2O_3 : C = 1:2:5.5$ and a milling period of 4 h. The average size of the agglomerates was 1.5–30 μm. The size of the TiO_2 crystallites in the precursor was determined by XRD and was found to be approximately 30 nm, which is equal to that of the initial TiO_2 particles. Fig. 4 shows the changes in the XRD peaks assigned to TiC (200) and TiB_2 (101). The initial molar composition of the precursor was $TiO_2 : B_2O_3 : C = 1:5:12.5$, and the reaction temperature was 1350 °C. The TiO_2 peaks rapidly disappeared and those due to TiC reached a maximum at 30 s after the start of the reaction. The TiB_2 peaks gradually increased with time, and no peaks that could be assigned to TiB, Ti_3B_4 and Ti_2B_5 were observed. The reaction was conducted at 1400, 1450 and 1500 °C, and the initial reaction rate of TiB_2 formation was determined for each temperature. From an Arrhenius plot of this data, the activation energy was calculated to be 340 kJ mol^{-1}, which is in agreement with the value for the production of NbB_2 by carbothermal reduction [14]. The formation of B_4C is negligible at

1400–1500 °C due to chemical equilibrium constraints. The present results suggest that carbothermal reduction of TiO_2 to TiB_2 proceeded as described by the reaction shown as Equation 2, which consists of the following steps:

$$TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO(g) \quad (3)$$

$$B_2O_3(l) + TiC(s) + 2C(s) \rightarrow TiB_2(s) + 3CO(g) \quad (4)$$

At higher temperatures, $B_2O_2(g)$, which is formed by the reaction shown as Equation 5, may participate in the carbothermal reductions shown in Equations 6 and 7.

$$B_2O_3(l) + C(s) \rightarrow B_2O_2(g) + CO(g) \quad (5)$$

$$B_2O_2(g) + TiC(s) + C(s) \rightarrow TiB_2(s) + 2CO(g) \quad (6)$$

$$2B_2O_2(g) + 5C(s) \rightarrow B_4C(s) + 4CO(g) \quad (7)$$

In the presence of TiO_2, the following reaction occurs:

$$B_4C + 2TiO_2 + 3C \rightarrow 2TiB_2 + 4CO(g) \quad (8)$$

The Gibbs free energy for B_4C forming via the reaction shown as Equation 1 at 1790 °C is –200 kJ mol^{-1}, and that for TiB_2 forming by the reaction shown as Equation 8 is –211 kJ mol^{-1} [22]. This suggests that TiB_2 is preferentially formed rather than B_4C.

Weimer *et al.* [11] expressed the carbon conversion due to the reaction shown as Equation 1 as follows, when carbon was the limiting component.

$$1 - \frac{[B_4C]}{[B_4C] + 0.1429[C]} = 1 - X = \exp\{-(kt)^3\} \quad (9)$$

where the brackets refer to the molar concentration of reactants, and t is the reaction period. The reaction rate coefficient k at 1790 °C was given as 0.48 s^{-1} [11]. The conversion, X, defined by Equation 9 is then calculated as 0.11 under the experimental conditions of the present study, i.e., 1790 °C and $t = 1$ s. This corresponds to a B_4C fraction of 8 wt % in the product. To examine the validity of the estimation, a precursor was prepared from H_3BO_3 and cornstarch ($B_2O_3 : C = 1:4$) which was subjected to carbothermal reduction using the vertical particulate transport reactor. The product recovered at the bottom of the reactor was washed with methanol to remove unreacted B_2O_3, and the B_4C content was determined by the XRD method. No substantial peaks of B_4C were detected in this experiment. If the reaction rate estimated from the result of Weimer *et al.* [11] is applied, then the B_4C weight fraction is, at most, 7 wt %. Thus, in the present study, the total carbon content in the product consisted predominantly of residual free carbon.

Fig. 5 (a and b) shows the morphology of the product particles after a carbothermal reduction at 1790°C. The precursor molar composition was TiO_2: $B_2O_3 : C = 1:2:5.5$, and the milling periods were 4 and 12 h. The average crystal-like size of the product particles was approximately 80 nm, which is larger than the original TiO_2 size of 30 nm, and the size was not significantly affected by the milling period.

Fig. 6 shows XRD patterns of the products as a function of milling period. The preparation method for the precursors and the reaction conditions were as described in Fig. 5. The peaks that correspond to TiC disappear when the milling time was greater than 8 h. A longer milling period increased the fraction of smaller agglomerates in the precursor, although the volume-averaged size of the particles remained unchanged. Thus, milling may increase the contact between the reactant TiO_2 and C particles. Fig. 7 shows the effect of carbon content in the precursor on the ratio of the relative intensity of the TiC (200) and TiB_2 (101) XRD peaks. The milling period was fixed at 4 h in this case. When the precursor molar composition was $TiO_2 : B_2O_3 : C = 1:2:6$, the yield of TiC reached its minimum.

To increase the conversion, the particles recovered at the reactor bottom were remixed with H_3BO_3, calcined (as described in the experimental section),

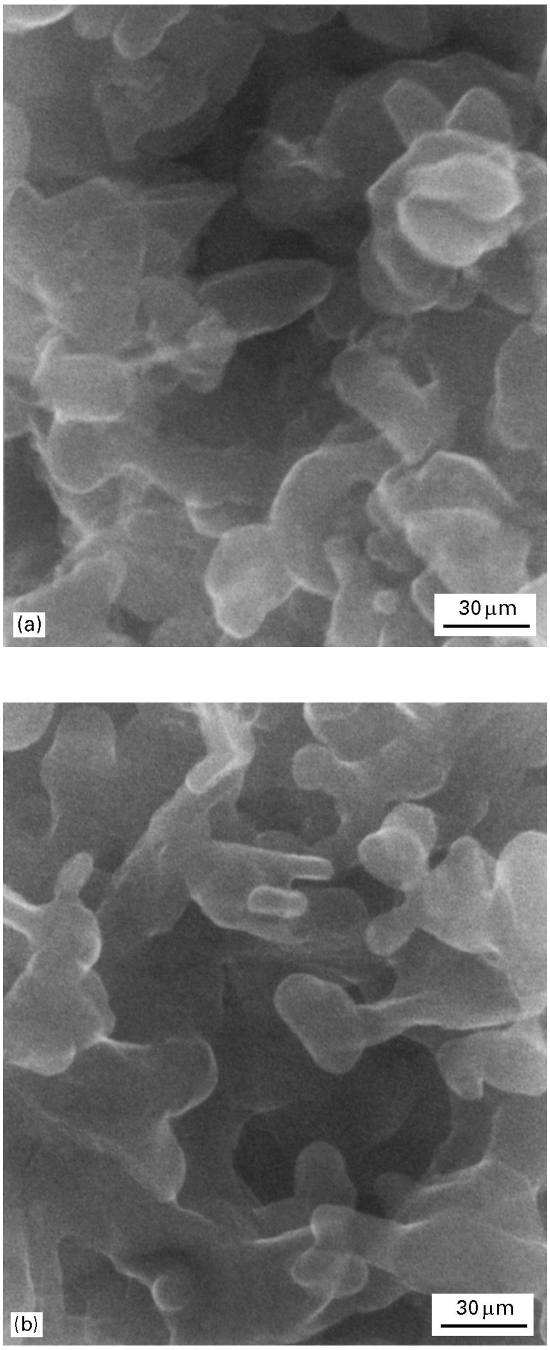

Figure 5 Morphology of the TiB_2 particles formed by rapid carbothermal reduction at 1791 °C. Milling period; (a) 4 h, (b)12 h.

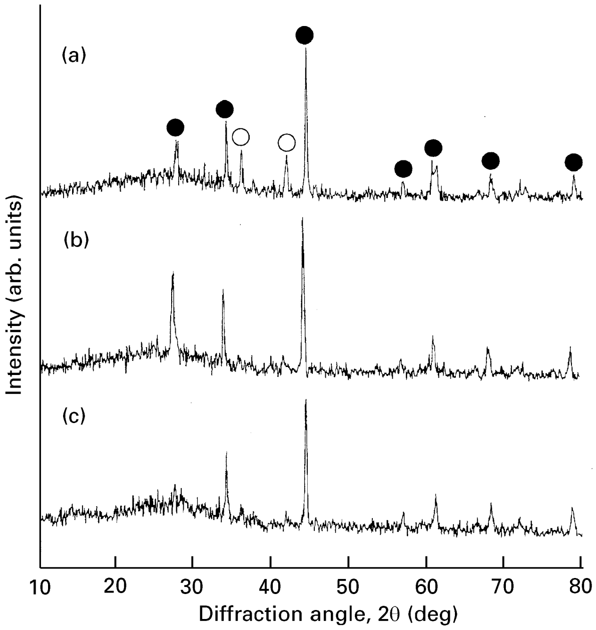

Figure 6 XRD patterns of products formed by rapid carbothermal reduction at 1791 °C. Milling period, (a) 4 h, (b) 8 h, (c)12 h. Key: (●) TiB_2 and (○) TiC.

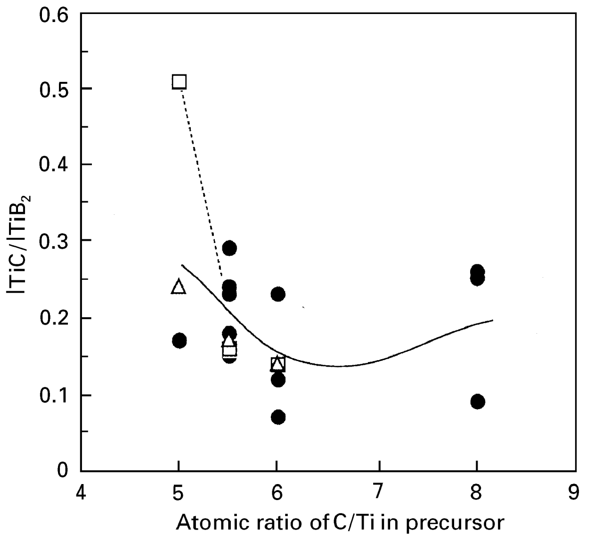

Figure 7 Effect of C/Ti atomic ratio in precursor on XRD intensity ratio of TiC to TiB_2. $TiO_2 : B_2O_3$ in precursor, (△) 1 : 1.5, (●) 1 : 2.0, (□) 1 : 2.5, on a molar basis.

pulverized and then fed into the reactor a second time. No differences were observed in the XRD patterns between the resulting product and the initial product. The conversion of TiO_2 to TiB_2 was practically complete after the initial reaction, and free carbon conversion was negligible at this temperature.

3.2. Carbon content in product particles

The content of residual carbon in the product particles was not greatly changed by repeating the reaction. An increase in the reaction temperature is effective in reducing residual carbon content by enhancing the reaction (shown as Equation 1), but a high reaction temperature gives sintering of the product particles as indicated by Weimer *et al.* [11] and Xiang *et al.* [12]. An improvement in the milling of precursors, on the other hand, was effective in that the residual carbon content was reduced from 10 to 5 wt % by extending the milling period from 4 to 12 h. This suggests that the contact between the solid reactants (TiO_2 and C) in the precursor is important for rapid carbothermal reduction. In the case of B_4C production by the reaction (shown as Equation 1), carbon is the limiting component and reacts with liquid or gaseous boron oxides. Unreacted boron oxides are easily removed by washing with methanol. In the case of TiB_2 production, solid-solid reactions are involved, TiO_2 particles rapidly react with carbon to give TiC, which then reacts with carbon to give TiB_2. Thus, the initial carbon content should be controlled in order to maximize the TiB_2 yield and to minimize any residual carbon.

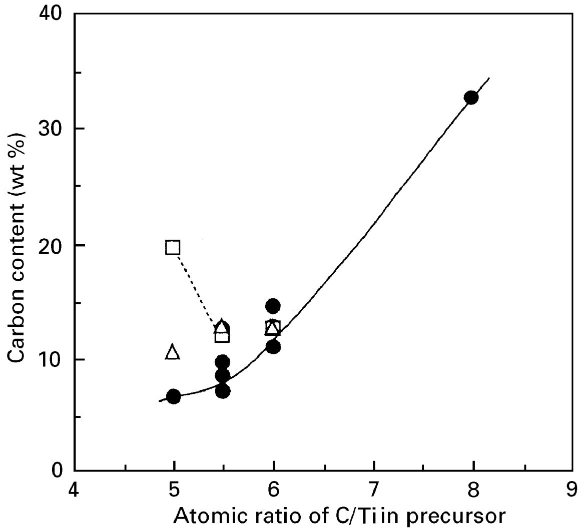

Figure 8 Effect of C/Ti atomic ratio in precursor on residual carbon content. Keys are the same as in Fig. 7.

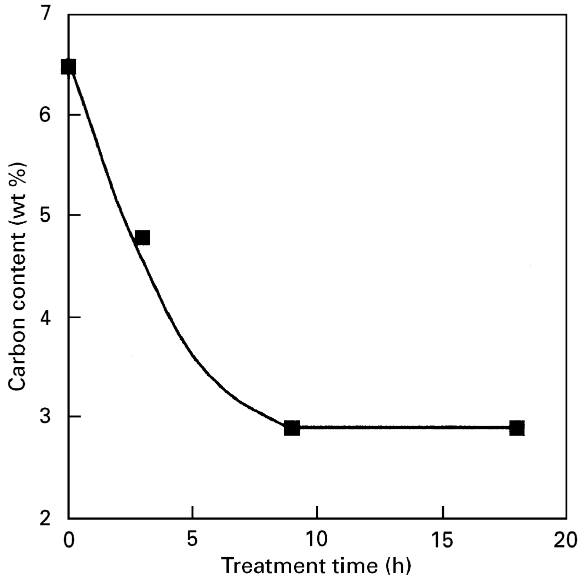

Figure 9 Effect of hydrogen treatment time on residual carbon content. Precursor molar composition, $TiO_2 : B_2O_3 : C = 1 : 2 : 5.5$, milling period, 8 h.

As described in the former section, the major portion of carbon in the product particles existed as amorphous free carbon. In the expectation of decreasing the carbon content, product particles were heat-treated in an H_2 atmosphere at 800°C for 3–18 h. Fig. 9 shows the effect of the treatment period on residual carbon content. The precursor possessed a molar composition of $TiO_2 : B_2O_3 : C = 1:2:5.5$ and was prepared with an 8 h milling. The free carbon in the product was reduced from 6.4 to 2.9 wt % as a result of a hydrogen treatment for 9 h.

4. Conclusions

Ultrafine TiB_2 particles were synthesized by rapid carbothermal reduction of precursor particles prepared with TiO_2, H_3BO_3 and cornstarch. When the precursor was composed of $TiO_2 : B_2O_3 : C = 1:2:5.5$, the carbon content was 5 wt %, and the crystalline particle size was 80 nm. The free carbon content in the product was reduced to 2.9 wt % by a heat treatment in an H_2 atmosphere at 800 °C for 9 h.

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