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Carbothermal synthesis of titanium carbide using ultrafine titania powders

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The synthesis of titanium carbide (TiC) by the carbothermal reduction of carbon coated titanium dioxide (TiO_2), a novel synthesis process, and titanium dioxide (TiO_2) mixed with carbon black was investigated. A high surface area (64 $m^2 g^{-1}$) TiO_2 powder consisting of anatase and rutile phases was used for starting powders. The carbon coated method is a two-step process that utilizes a precursor derived from decomposing propylene (C_3H_6) and depositing carbon on the TiO_2 particles. TiO_2 powders were also mechanically mixed with carbon black for comparison. Both starting precursors and mixtures were reacted in a tube furnace for 2 and 4 h at temperatures of 1100 °C to 1550 °C under 1 l min^{-1} flowing argon. The TiC powders were characterized using thermogravimetric analysis (TGA), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analyser, chemical analysis (oxygen and carbon) and transmission electron microscopy (TEM). The carbon coating process provides high contact area between the reactants which results in a TiC product with lower oxygen content (0.6 wt%), finer particle size (0.1μm), and uniform shape when synthesized at 1550 °C for 4 h.

1. Introduction

Metal carbides, nitrides and carbonitrides are the leading advanced engineering ceramics used in metalworking, electrical and electronic, automotive, and refractory industries. This is due to their high temperature strength retention, excellent oxidation resistance, low thermal expansion coefficient, high wear resistance, high melting point and light weight. TiC has many applications in key high technologies from mechanical and chemical industries to electronics [1]. TiC combines the advantages of a high melting point (3260 °C) and hardness (Knoop's = 32.4 GPa) with a low density (4.93 g cm^{-3}). It also exhibits a high resistance to both oxidation and corrosion [2].

TiC is extensively used in various branches of machine construction due to its high strength and hardness [3]. It is useful for the manufacturing of cutting tools, grinding wheels, coated cutting tips and coated steel press tools [4]. TiC can also be used as a substitute for tungsten carbide (WC), a common machining material, due to its similar properties of high hardness, melting point, and wear resistance. Currently 10% of the world's consumed cobalt (Co) is used as binder material for WC components [5]. TiC compounds can use nickel (Ni) as a binder which has more stable sources and costs only half as much as Co [5, 6].

Fabrication of TiC ceramics involves a series of processing steps that are designed to produce dense components. Processes include powder preparation, shaping, sintering, and finishing. Each step has the potential for introducing a detrimental heterogeneity or flaw which will persist during further processing or develop into a new heterogeneity during sintering. If reliable TiC components are to be fabricated, one must ensure that heterogeneities are eliminated from the powders and will not be reintroduced in subsequent steps. In addition, the cost of high quality (high purity, high surface area, spherical) powder is a major factor hindering the wide commercialization of TiC, TiN, and Ti(C,N) components. Present methods of synthesizing high quality powders require expensive steps that yield only small quantities of product.

A number of processes exist for synthesizing TiC powders. Each method has varying characteristics of particle size and distribution, morphology, state of agglomeration, chemical purity, and stoichiometry. TiC powder is commercially produced primarily by the reduction of TiO_2 by carbon, especially carbon black, in a temperature range between 1700–2100 °C [7] as shown by Equation 1

$$TiO_2(s) + 3C(s) = TiC(s) + 2CO(g) \qquad (1)$$

Because the reactants exist as separate particles, the extent of this reaction is limited by the contact area between the reactants and the distribution of the carbon within the TiO_2. These limitations result in a product that contains unacceptable quantities of unreacted carbon and oxides of titanium. The TiC powder produced has a relatively wide size range, due to grain growth and bonding together of the individual particulate during the reduction reaction and therefore requires subsequent milling. For this process, reaction time is typically very long (10–20 h), and

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powders produced generally have undesirable inhomogeneities due to diffusion gradients established during the reduction reaction [8].

The direct carburization method exploits the reaction between titanium and carbon as shown in Equation 2

$$Ti(s) + C(s) = TiC(s) \tag{2}$$

TiC synthesis starting from elemental Ti and C is demanding and has limited applications. It is difficult to make submicron Ti metal particles. Once such particles are produced, they are pyrophoric and difficult to handle [9]. This method requires 5–20 h to complete, produces strongly agglomerated powders that require extensive milling to yield fine powders, and requires chemical purification to remove impurities from mill wear. In addition, the high cost of the elemental metal source leads to a relatively expensive product.

Another method is based on the chemical reaction between $TiCl_4$, H_2, and C [1], as shown by Equation 3

$$TiCl_4(g) + 2H_2(g) + C(s) = TiC(g) + 4HCl(l) \tag{3}$$

The reaction is driven in contact with an incandescent tungsten or carbon filament. Either single crystal or polycrystalline TiC is grown directly on the filament. This method severely limits the quantity and sometimes the quality of the resulting powder. In addition, special precautions have to be taken because the precursor $TiCl_4$ and the product HCl are very corrosive.

Self-propagating high temperature synthesis can also be used to produce TiC through exothermic reactions [10]. Fine particles of titanium are highly reactive when heated to moderate temperatures. Titanium and carbon have sufficiently high heats of reaction so that after ignition a combustive wave propagates throughout the reactants converting them into TiC. The reactions are extremely rapid, often being completed in less than a second. Again very fine, pure titanium is needed and large quantities are not produced.

There are a few experimental methods for producing TiC powder. One method uses TiS_2 and C to produce TiC [1] according to the reaction in Equation 4.

$$TiS_2(s) + 2C(s) = TiC(s) + CS_2(g) \tag{4}$$

To initiate this chemical reaction, the mixture has to be heated to 2000 °C under high vacuum to avoid oxidation. Other experimental methods include direct carburization synthesis by multipulse laser treatment of titanium samples in ambient CH_4 gas [9]. These processes use large amounts of energy, are costly, and still do not yield powders with the desired set of physical and chemical characteristics.

It is therefore apparent that a need is present for a process for producing TiC powder with uniformity, speed, and economy. In accord therewith, a primary object of the present paper is to introduce a novel carbon coated synthesis method for producing submicron, high purity, nonagglomerated TiC powders. A detailed description of this method and comparison with commercial processes are presented. The physical, chemical and crystalline nature of the produced powders and the effect of process variables are discussed.

2. Experimental procedure

2.1. Starting TiO_2 powders

The starting titania powders were a very high surface area TiO_2 from Degussa (P-25, Degussa Corp., Ridgefield, NJ). The transmission electron microscopy (TEM) micrograph of the Degussa P-25 TiO_2 particles (Fig. 1) showed that it has an average particle size of 20 nm. The equivalent spherical diameter of the particles was determined to be 22 nm, as calculated from a measured Brunauer–Emmett–Teller (BET) surface area of 64 $m^2 g^{-1}$. X-ray diffraction (XRD) of the Degussa P-25 TiO_2 (Fig. 2) powders showed that multiphases of anatase and rutile existed with a ratio of 70 and 30%, respectively.

2.1.1. Cracking of C_3H_6

As a preliminary step, the formation of the condensed phase of carbon by the pyrolysis of C_3H_6 was studied by obtaining an equilibrium composition, with one mole of C_3H_6 gas, using computer software (HSC

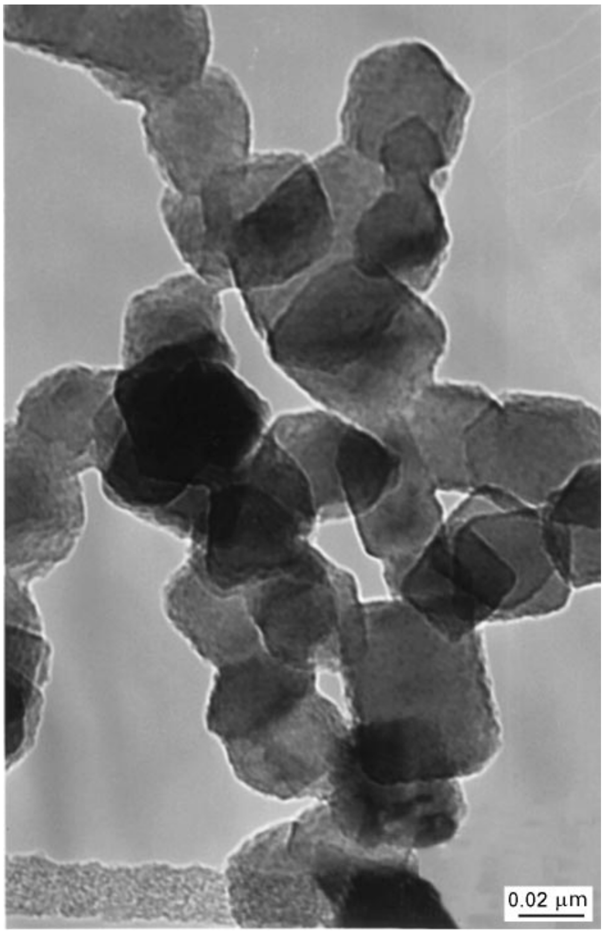

Figure 1 TEM micrograph of TiO_2 powder.

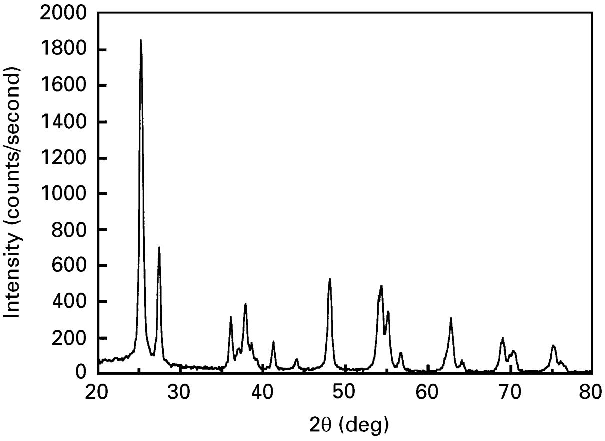

Figure 2 XRD pattern of TiO_2 powder.

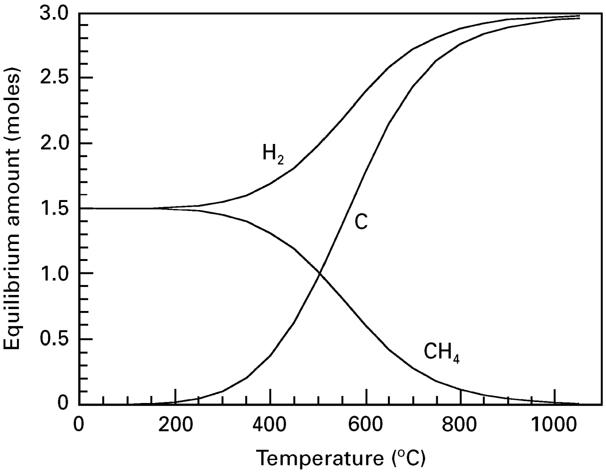

Figure 3 Equilibrium composition of major products out of 1 mole of C_3H_6 gas at 2.75×10^5 Pa pressure.

Chemistry, Outokumpu Oy, Pori, Finland) based on Gibbs free energy change as a function of temperature. Fig. 3 shows the equilibrium composition of the major products produced from 1 mole of C_3H_6 gas at 2.75×10^5 Pa pressure. As shown in Fig. 3, the reaction in Equation 5.

$$2C_3H_6(g) = 3C(s) + 3CH_4(g) \tag{5}$$

is dominant at low temperatures, while the formation of high purity condensed phase of carbon is accelerated at high temperatures, according to the reaction in Equation 6

$$C_3H_6(g) = 3C(s) + 3H_2(g) \tag{6}$$

Based on these calculations the pyrolysis of hydrocarbon (C_3H_6) gas was determined to be 600 °C for a low density, amorphous, and highly porous carbon coating step.

2.1.2. Preparation of carbon coated precursors

The precursor powders were prepared using a rotating coating apparatus, consisting of a 10 cm i.d. × 35 cm long stainless steel vessel used for preparing the pyrolytic carbon coated TiO_2 particles utilizing propylene (C_3H_6) as the coating gas. About 60 g of TiO_2 powder were placed in the vessel and the vessel was evacuated, purged with argon, and again evacuated to a moderate vacuum level, using a rotary vacuum pump. Then the vessel was heated to 600 °C, kept at 600 °C for 30 min, and filled with propylene gas until the pressure reached 2.75×10^5 Pa. Thermal cracking of propylene increased the internal vessel pressure to approximately 3.44×10^5 Pa upon initiation of the carbon coating. After approximately 20 min the remaining gas was released and the vessel was filled with fresh propylene. After every third cycle the vessel was evacuated, purged with argon, and again evacuated before filling with propylene. The coating step was continued until 32–34 wt % carbon was deposited, which required about 18 cycles. When a portion of the coating process was finished the vessel was evacuated, filled with argon and allowed to cool to room temperature.

The weight percentage of the carbon in the precursor was determined by using thermogravimetric analysis in air. A small sample of the carbon coated powder was placed in a crucible with the weight of the sample and crucible being known. The crucible was then placed in a box furnace and the carbon coating was oxidized at 750 °C for 6 h. The crucible was then weighed to determine the weight loss and the weight percent of carbon in the precursor was calculated.

2.1.3. Preparation of TiO_2 and carbon black mixtures

TiO_2 and carbon black (Monarch 880, Cabot, Waltham, MA) samples were prepared by adding 6.63 g (66.3 wt %) of TiO_2 with 3.37 g (33.7 wt %) of carbon black (particle size = 16 nm, surface area of $220\,m^2\,g^{-1}$). The TiO_2 and carbon mixtures were placed in a plastic container (i.d. = 5 cm and height = 7 cm) and milled with two polymer balls for 30 min in a Spex (Model 8000 Mixer/mill, Meutuchen, NJ) mixer.

2.1.4. Synthesis of TiC powders

The carbon coated TiO_2 precursors and the TiO_2 with carbon black mixtures were then synthesized in a tube furnace (Model CTF 17/75/300, Carbolite, Hope, Sheffield, UK) with an i.d. of 70 mm. Ten grams of a given sample for each temperature (1200, 1300, 1400, 1500 and 1550 °C) were placed in a graphite crucible (i.d. = 65 mm and length = 10 cm). The furnace was first evacuated before a flowing stream of argon at $1\,l\,min^{-1}$ was supplied. The TiC powders were then produced by promoting a carbothermal reduction within the carbon coated titania and mixed titania and carbon black samples. The samples were synthesized at temperatures of 1100, 1200, 1300, 1400, 1500, and 1550 °C for two hours to investigate reaction mechanisms and determine an optimal reaction temperature. A heating rate of 4 °C/min and a cooling rate of 4 °C/min was used.

2.2. Characterization of synthesized TiC powders

The weight loss of all the TiC powders was measured after the powders were allowed to cool and removed from the tube furnace. From Equation 1, the percentage weight loss for the stoichiometric reaction was calculated to be 48.3%. A weight loss less than this amount indicates an incomplete reaction, whereas greater weight loss indicates the presence of volatile species.

The samples were then subjected to XRD (Model DMAX-B, Rigaku, Tokyo, Japan) for the study of phase evolution, using CuK_α radiation. A gram of each sample was X-rayed in powder form at a scanning speed of $2°\text{–}2\theta\ \mathrm{min}^{-1}$ at an increment of 0.05 from 10 to 90°.

The surface areas of the powders were measured using a BET gas adsorption surface area analyser (Micromeritics, Gemini 2360, Nocross, GA). Approximately 0.3 to 0.5 g of powder were placed in a test tube and allowed to degas for 2 h at 175 °C in flowing nitrogen. This removes contaminants such as water vapour and adsorbed gases from the samples. After a sample was degassed, the surface area was analysed and a BET multipoint surface area report was given based on the amounts of gases absorbed and the corresponding pressures.

TEM (Model FA 7100, Hitachi Inc., Tokyo, Japan) studies were also performed. A small amount (0.5 g) of each sample was diluted in 25 ml of normal butanol, a slightly viscous alcohol, and sonicated for 30 min. Three to four drops from an eye dropper of the sonicated samples were then placed on copper grids with holly carbon coated formvare. The samples were placed in a vacuum oven to dry before examining.

Oxygen and total carbon content of the produced powders were determined by Leco (St. Joseph, MI). Oxygen was analysed by infrared detection in a Leco R0416DR induction furnace, while total carbon content was determined by ignition in a Leco C200 induction furnace, which analysed the evolved CO_2 calorimetrically.

The lattice parameter of the TiC reaction product was determined by X-ray powder diffractometry with CuK_α radiation. For calibration of errors in scanning angle, submicron nickel powder was used as an internal standard. The TiC sample (65 wt %) and internal standard (35 wt %) were mixed using a mortar and pestle and then scanned from 25 to 150 degrees (2θ) with a 0.5° scanning speed. The lattice parameter value, a, associated with each peak position was calculated and plotted as a function of $\cos^2\theta$ in order to determine the least square line as in Equation 7.

$$a = a_0 + K\cos^2\theta \tag{7}$$

where a_0 is the extrapolated true value of a when θ approaches 90 degrees and K is the slope of the least square lines.

3. Results and discussion

Fig. 4 shows the XRD pattern of the carbon coated titania precursors. In Fig. 4, all peaks correspond to the TiO_2 anatase and rutile phases, implying pyrolytic amorphous carbon was deposited. Fig. 5 shows TEM micrograph of the carbon-coated TiO_2 precursors. The darker areas are TiO_2 particles and the lighter areas surrounding the darker areas are the carbon coating. As shown in Fig. 5, an extremely uniform coating of pyrolytic carbon on titania is apparent. The BET surface area of the TiO_2 powder decreased from $64\ \mathrm{m}^2\,\mathrm{g}^{-1}$ to $42\ \mathrm{m}^2\,\mathrm{g}^{-1}$ after being coated. These results showed that an uniform, highly porous and low density carbon coating can be deposited at 600 °C on TiO_2 particles by using C_3H_6 gas. This process forms

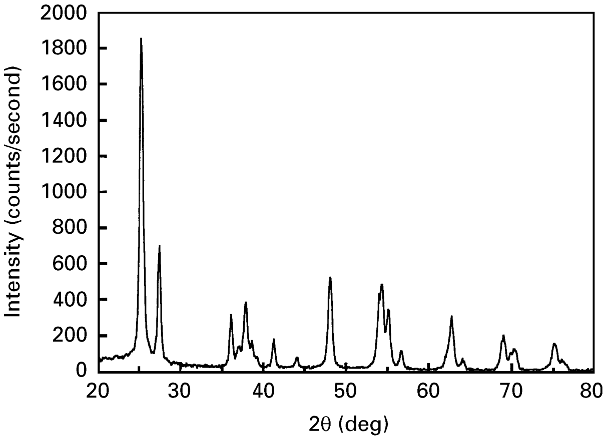

Figure 4 XRD pattern of TiO_2 powder coated with carbon.

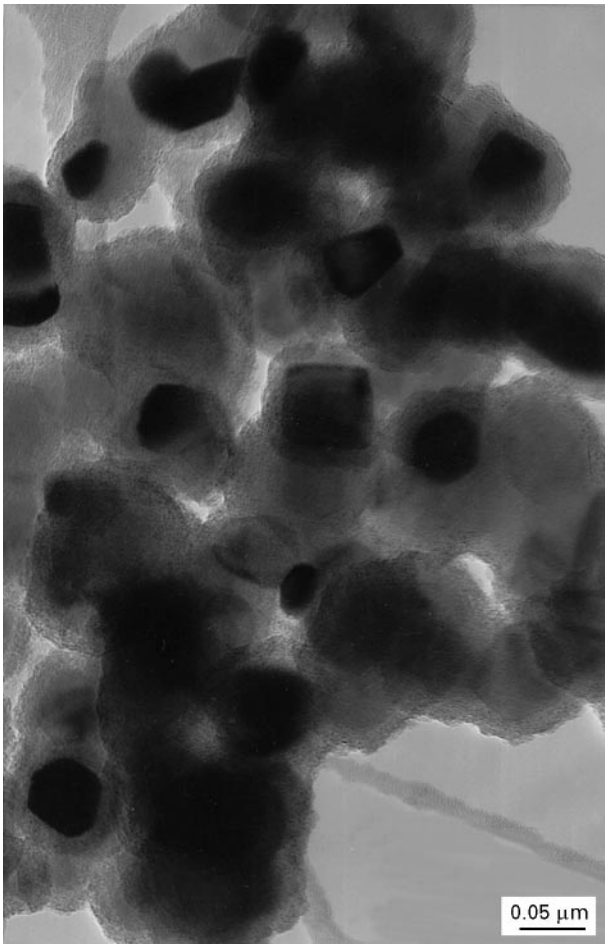

Figure 5 TEM micrograph of TiO_2 powder coated with carbon.

an intimate mixing of the reactants (carbon and TiO_2) with high surface contact between the carbon and TiO_2. This also results in a continuous supply of carbon monoxide during the reaction which makes the reduction of TiO_2 possible by gas phase reduction. In addition, these precursors are capable of producing high purity TiC particles at low temperatures, because the carbon source is a hydrocarbon gas. Therefore impurities, such as iron which is ordinarily found in the commercial carbon material are eliminated. The use of the precursor results in the production of submicron and uniform TiC particles, because the agglomeration of the oxides of titanium is also inhibited by a carbon layer.

Fig. 6 shows TEM micrograph of the TiO_2 mixed with carbon black. As shown in Fig. 6, the contact area between the TiO_2 and carbon black is inconsistent; therefore, there will not be a continuous supply of CO for oxide reduction and carbon for CO generation. This leads to reduction reactions reversing, agglomeration and particle growth. A non-uniform product with various sizes, shapes, and purity will result.

Fig. 7 shows the weight loss for the carbon coated TiO_2 and TiO_2 mixed with carbon black. The weight loss data illustrates that a reaction temperature of 1500 °C for 2 h is required to accomplish the acceptable degree of reaction. At 1200 °C the carbon-coated TiO_2 has greater weight loss than the mixed TiO_2 with carbon black. The mixed powder shows greater weight loss at 1300 and 1400 °C, due to its inconsistent mixing and by delaying reactions to higher temperatures. At 1500 °C the carbon-coated and mixed TiO_2 show an identical weight loss of 48% which indicates a complete reaction.

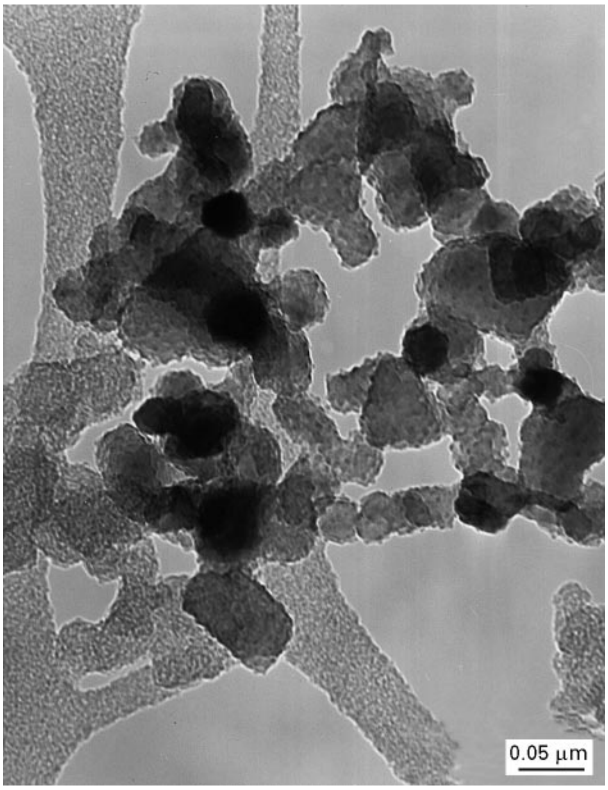

Figure 6 TEM micrograph of TiO_2 powder mixed with carbon black.

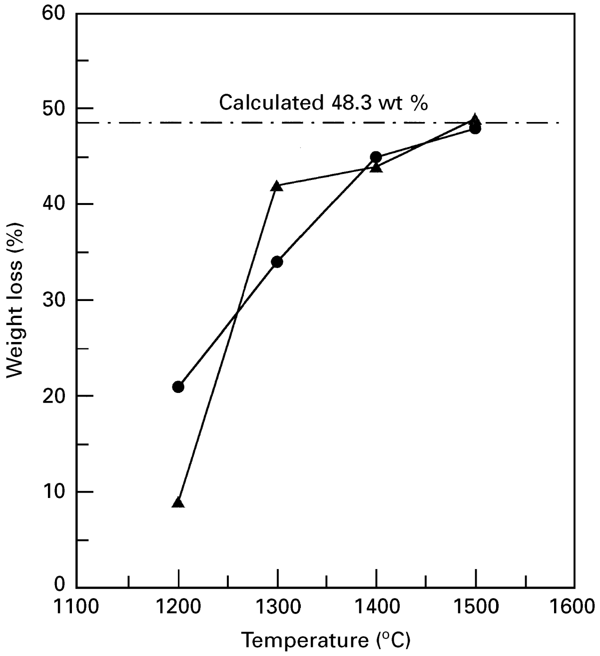

Figure 7 Weight loss versus temperature for coated (●) and mixed (▲) TiO_2 powder over 2 h.

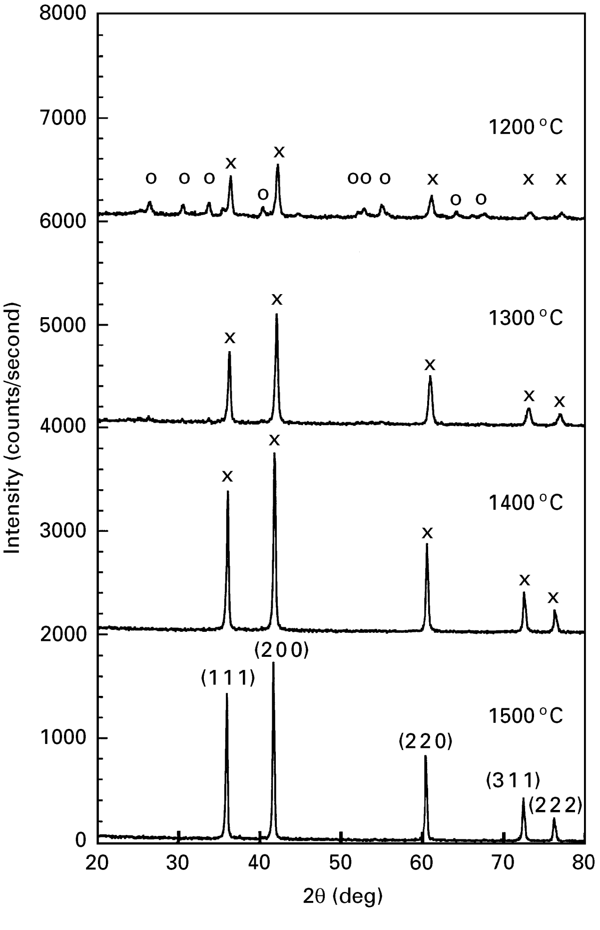

Figure 8 XRD results of reaction products from TiO_2 powder coated with carbon and synthesized at 1200–1500 °C for 2 h in flowing argon $1\,l\,min^{-1}$. (○) Ti_3O_5; (×) TiC_xO_y.

The XRD patterns in Fig. 8 show the formation of TiC powders synthesized from the carbon coated TiO_2 precursor at various temperatures. Phases in the

XRD pattern for the powder produced at 1200 °C were determined to be Ti_3O_5 and TiC_xO_y. At 1300 °C lower oxides of titanium disappeared and TiC_xO_y formation was completed. At 1400 °C no oxide phase was identified, while TiC peak intensities increased with temperature as the purification of TiC_xO_y into TiC started. The XRD pattern at 1500 °C shows sharp TiC peaks as the purification of TiC_xO_y into TiC continued.

Fig. 9 shows the XRD patterns for the formation of TiC powders synthesized from TiO_2 mixed with carbon black at various temperatures. At 1200 °C, the mixed powder showed more oxide phases than the carbon coated powder. These phases were identified to be Ti_3O_5, and Ti_2O_3. TiC_xO_y formation was not present until 1300 °C for the powders. On the other hand, TiC_xO_y formation was present at 1200 °C for the powders synthesized using carbon coated precursor. The lack of a consistent source of C and CO, due to non-uniform mixing, is expected to delay reduction reactions and TiC_xO_y formation until higher temperatures. At 1300 °C, the mixed powders had no presence of lower oxides of titanium, yet TiC_xO_y formation was completed as in the carbon-coated powder. At 1400 °C, the TiC_xO_y lost more oxygen as the purification of TiC proceeded. At 1500 °C, the TiC peaks increased, revealing an even more pure TiC powder was being formed.

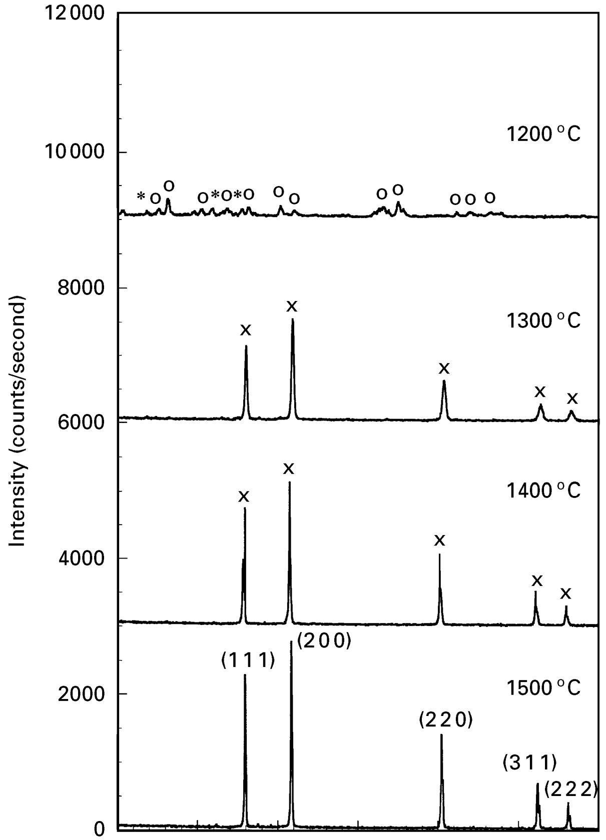

Figure 9 XRD results of reaction products from TiO_2 powder mixed with carbon black and synthesized at 1200–1500 °C for 2 h in flowing argon 1 l min^{-1}. (O) Ti_3O_5; (*) Ti_2O_3; (×) TiC_xO_y.

The carbothermal reduction of TiO_2 may be described by the overall reaction, as shown previously in Equation 1, which is actually the sum of a more complex set of reactions. The initial stage of the reaction for the carbon-coated powders, which starts at about 900 °C, is the reduction of TiO_2 to its lower oxides, as shown in Equations 8 and 9

$$a\mathrm{TiO_2(s)} + b\mathrm{C(s)} = c\mathrm{Ti}_x\mathrm{O}_y\mathrm{(s)} + d\mathrm{CO(g)} \quad (8)$$

$$a\mathrm{TiO_2(s)} + b\mathrm{CO(g)} = c\mathrm{Ti}_x\mathrm{O}_y\mathrm{(s)} + d\mathrm{CO_2(g)} \quad (9)$$

The lower oxides were not identifiable below 1000 °C, but at 1000 °C Ti_3O_5 was identified in the X-ray pattern. Ti_2O_3 was not present in any of the XRD patterns. According to the XRD patterns, Ti_3O_5 is converted into TiC_xO_y between 1100 and 1150 °C, as shown in Equations 10 and 11.

$$a\mathrm{Ti_3O_5(s)} + b\mathrm{CO(s)} = c\mathrm{TiC}_x\mathrm{O}_y\mathrm{(s)} + d\mathrm{CO_2(g)} \quad (10)$$

$$a\mathrm{Ti_3O_5(s)} + b\mathrm{C(s)} = c\mathrm{TiC}_x\mathrm{O}_y\mathrm{(s)} + d\mathrm{CO(g)} \quad (11)$$

Carbon dioxide is reduced by the carbon that is present in the system according to Equation 12.

$$\mathrm{CO_2(g)} + \mathrm{C(s)} = 2\mathrm{CO(g)} \quad (12)$$

TiC can be formed by TiC_xO_y reacting with C or CO, as shown in Equations 13 and 14.

$$a\mathrm{TiC}_x\mathrm{O}_y\mathrm{(s)} + b\mathrm{CO(g)} = c\mathrm{TiC(s)} + d\mathrm{CO_2(g)} \quad (13)$$

$$a\mathrm{TiC}_x\mathrm{O}_y\mathrm{(s)} + b\mathrm{C(s)} = c\mathrm{TiC(s)} + d\mathrm{CO(g)} \quad (14)$$

In these reactions, carbon is either a CO_2 reducer or a CO generator which keeps the CO_2/CO ratio low enough to make the reduction of TiO_2 possible by gas phase reduction. Because the extent of the reactions is limited by the contact area between the reactants and continuous supply of CO, the intimate contact of carbon with TiO_2, Ti_xO_y and CO_2 is essential during reduction in order for complete conversion of TiO_2 into TiC.

The initial stage of the reaction for the mixed powders is the reduction of TiO_2 to lower oxides. Eventually TiO_2 is reduced to Ti_3O_5, the same as shown in Equations 8 and 11, but at around 1150 °C. Ti_3O_5 is then reduced to Ti_2O_3, Equations 15 and 16, at about 1175 °C

$$2\mathrm{Ti_3O_5(s)} + \mathrm{C(s)} = 3\mathrm{Ti_2O_3(s)} + \mathrm{CO(g)} \quad (15)$$

$$2\mathrm{Ti_3O_5(s)} + \mathrm{CO(g)} = 3\mathrm{Ti_2O_3(s)} + \mathrm{CO(g)} \quad (16)$$

The equilibrium CO_2/CO ratio is maintained, as shown previously in Equation 12. Ti_2O_3 is finally reduced into TiC_xO_y, as shown in Equations 17 and 18

$$a\mathrm{Ti_2O_3(s)} + b\mathrm{CO(g)} = c\mathrm{TiC}_x\mathrm{O}_y\mathrm{(s)} + d\mathrm{CO_2(g)} \quad (17)$$

$$a\mathrm{Ti_2O_3(s)} + b\mathrm{C(s)} = c\mathrm{TiC}_x\mathrm{O}_y\mathrm{(s)} + d\mathrm{CO(g)} \quad (18)$$

This results in TiC powder that contains unacceptable quantities of oxygen and unreacted carbon. This is due to interruption of intimate contact of Ti_xO_y and C in the reduction reactions. Ti_2O_3 is formed when there is a lack of carbon or CO and the formation of TiC_xO_y

from Ti_3O_5, which is not favourable, prolongs the reaction. The reaction rate is extremely slow and complete reaction is practically impossible to complete by this mechanism.

The BET surface area measurements were made to obtain information about the reaction mechanism and the particle size of the resulting powders as a function of the reaction temperature. As can be seen from Fig. 10, the BET surface area of the reaction products, from the carbon coated and mixed TiO_2 powders, increased with reaction temperature to a maximum at 1300 °C and then decreased as the reaction temperature increased. The increase in BET surface area from 1100 to 1300 °C may be related to the formation of the lower oxides of titanium. The XRD pattern of the carbon-coated TiO_2 powders showed that unidentified and Ti_3O_5 phases exist below 1300 °C. Since the particle size of the carbon in the mixed powders would be constant, TiO_2 must be decreasing in size for the powders to increase in surface area. The decrease in the BET surface area from 1300 to 1500 °C implies the particle growth of TiC_xO_y. The mixed powders have higher surface area at 1100, 1200 and 1300 °C because of the free carbon content. At 1400 °C the surface area of powders produced from mixed TiO_2 with carbon precursor is lower due to the inconsistent reaction methods and higher at 1500 °C due to unreacted carbon.

TEM was used to investigate the particle size, size distribution, shape and degree of agglomeration. Micrographs were taken at different stages of the carbothermal reduction reaction of TiO_2 and C into TiC. Fig. 11 is a TEM micrograph of reaction products from TiO_2 powder coated with carbon and reacted at 1200 °C for 2 h. There are many different particle sizes shown in the micrograph which are the lower oxides of titanium present (Ti_3O_5 according to XRD results). While the carbothermal reduction reaction of TiO_2 into TiC is in the initial stages, the Ti_3O_5 and TiC_xO_y are present, according to the XRD pattern in Fig. 8. The small transparent particles are unreacted carbon that has not been consumed at this stage of the reaction. Particles range in size from 0.01 µm unreacted carbon to 0.1 µm (Ti_3O_5 and TiC_xO_y). Fig. 12

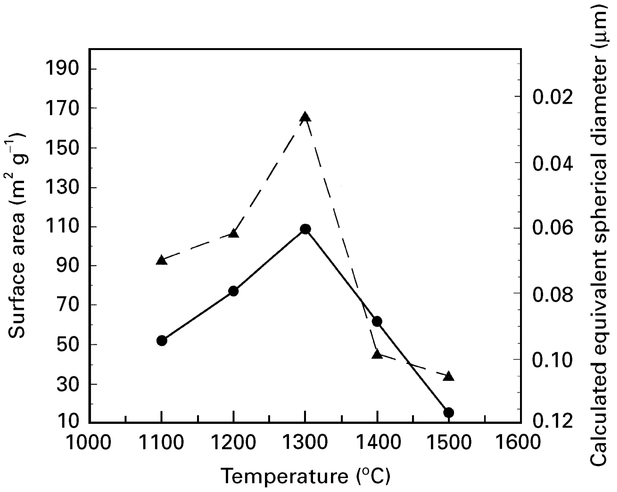

Figure 10 BET Surface area versus temperature for coated (●) and mixed (▲) TiO_2 powder.

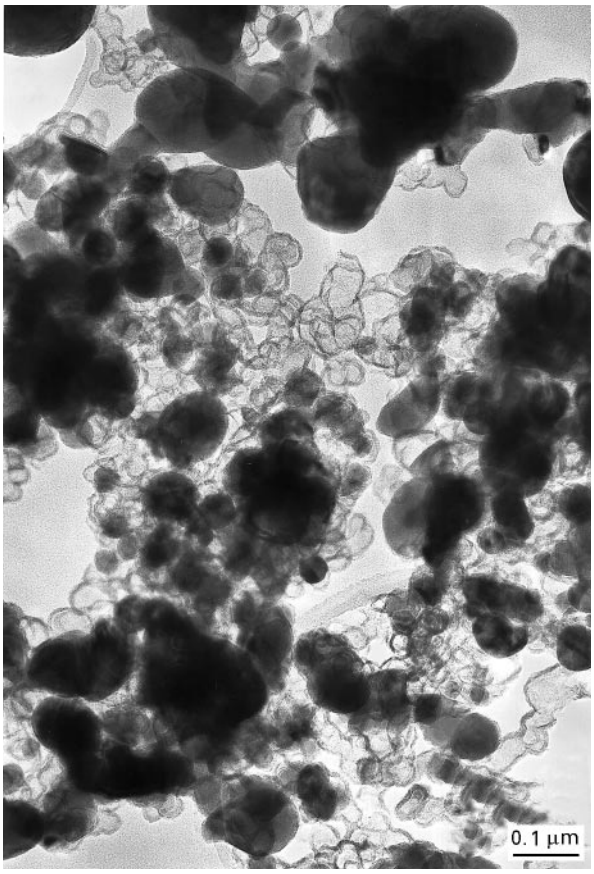

Figure 11 TEM micrograph of TiO_2 coated with carbon reaction product at 1200 °C for 2 h in flowing argon.

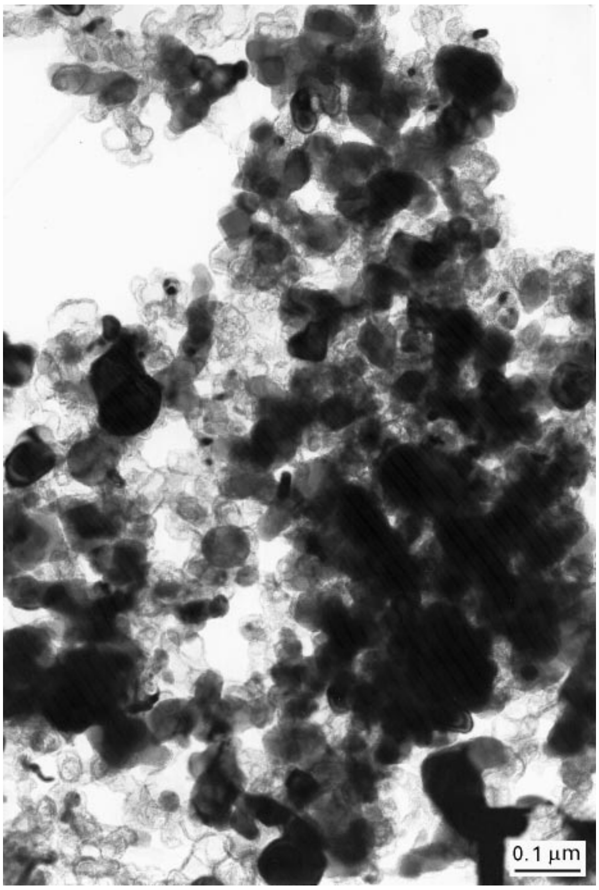

Figure 12 TEM micrograph of TiO_2 coated with carbon reaction product at 1300 °C for 2 h in flowing argon.

is a TEM micrograph of the reaction products from TiO_2 powder coated with carbon and reacted at 1300 °C for 2 h. The particles shown in the micrograph are all about the same size with the exception of the unreacted carbon. Almost all the particles are in the form of TiC_xO_y at this stage of the reaction. The XRD results in Fig. 8 identified that TiC_xO_y is the only phase present. Unreacted carbon can still be seen and will be needed later in the reaction to further reduce the TiC_xO_y into TiC. Particles range in size from 0.01 μm (unreacted carbon) to 0.05 μm (TiC_xO_y). Fig. 13 is a TEM micrograph of the reaction products from TiO_2 powder coated with carbon and reacted at 1400 °C for 2 h. As shown by the micrograph, the particles are starting to coarsen and the amount of free carbon present is reducing. The reaction is nearing its final stage, but is not completed. The XRD pattern in Fig. 8 shows sharper peaks of TiC_xO_y, which proves there is less TiO in solution and unreacted carbon present. The particles do not appear to be as spherical and range in size from 0.01 μm (unreacted carbon) to 0.1 μm (TiC_xO_y). A slight degree of agglomeration is present, but most particles are likely just overlapping each other. Fig. 14 is a TEM micrograph of reaction products from TiO_2 powder coated with carbon and reacted at 1500 °C for 2 h. There is hardly any free carbon present and it is believed that the reaction has completed. The XRD results in Fig. 8 and chemical analysis (oxygen and total carbon) confirmed that a pure TiC has been produced. The particles have a narrow size distribution and are loosely agglomerated. The particles are mostly spherical with some edges and range in size from 0.1 μm to 0.3 μm.

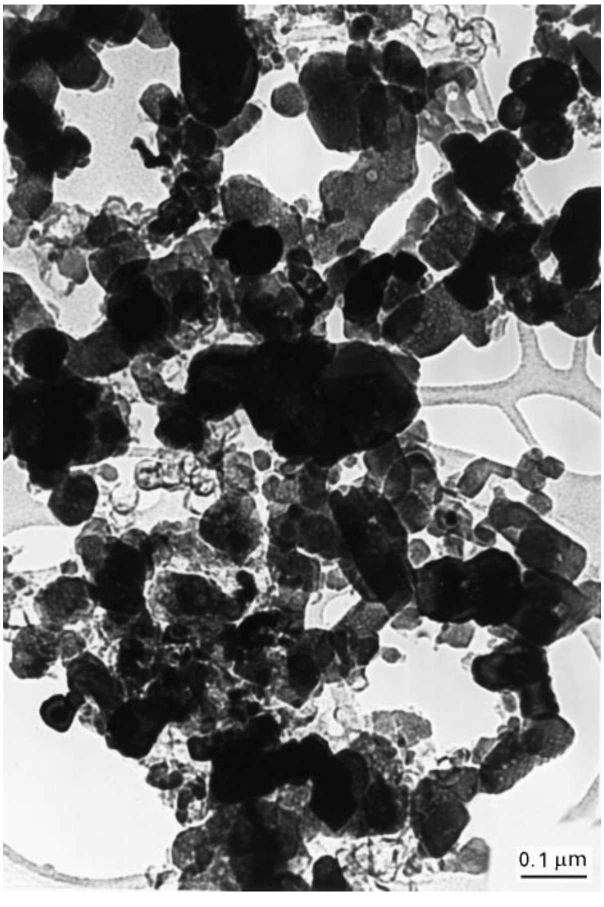

Figure 13 TEM micrograph of TiO_2 coated with carbon reaction product at 1400 °C for 2 h in flowing argon.

Figure 14 TEM micrograph of TiO_2 coated with carbon reaction product at 1500 °C for 2 h in flowing argon.

Fig. 15 shows TEM micrograph of synthesized powders from TiO_2 coated with carbon at 1550 °C for 4 h. As it can be seen from Fig. 15, the produced TiC powders have fine particle size (0.1–0.25 μm), narrow particle size distribution, and are loosely agglomerated. The resultant TiC powders have oxygen content of 0.6 wt % and 22.67 wt % total carbon with a lattice parameter of 0.433 nm. A small amount of oxygen exists as TiO in solid solution with TiC. The decrease in oxygen weight percent verifies the purification of TiC, however, it is impossible to completely eliminate oxygen from such fine TiC powders. The weight percent of oxygen decreased for the powders as temperature and time increased. The theoretical amount of carbon for TiC is 20.05 wt %. An excess amount of 2.62 wt % initial carbon (33.7 wt %) was used to ensure carbon was always available and the reduction reaction would not reverse.

Fig. 16 is a TEM micrograph of the reaction products from TiO_2 powder mixed with carbon black and reacted at 1200 °C for 2 h. The inconsistent mixing is apparent at this stage of the reaction, since agglomerates of particles and unreacted carbon can be seen. According to the XRD results in Fig. 9, the agglomerates consist of Ti_2O_3 and Ti_3O_5 pattern. Particles

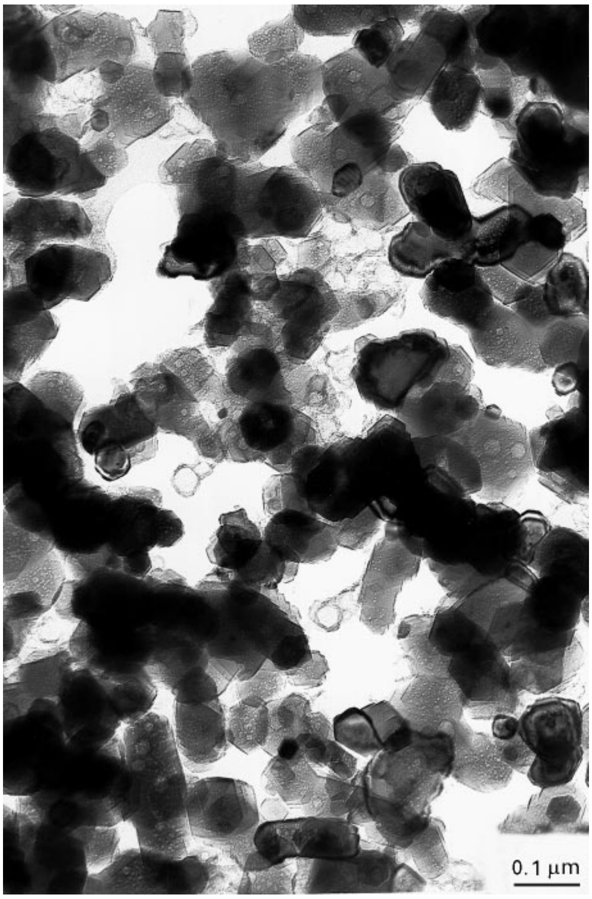

Figure 15 TEM micrograph of TiO_2 coated with carbon reaction product at 1550 °C for 4 h in flowing argon.

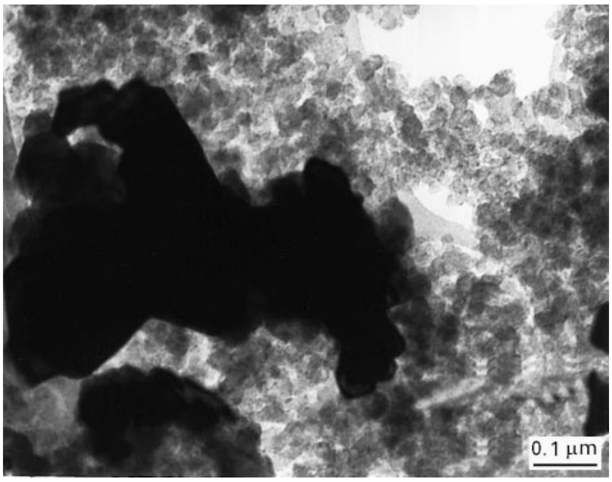

Figure 16 TEM micrograph of TiO_2 mixed with carbon black reaction product at 1200 °C for 2 h in flowing argon.

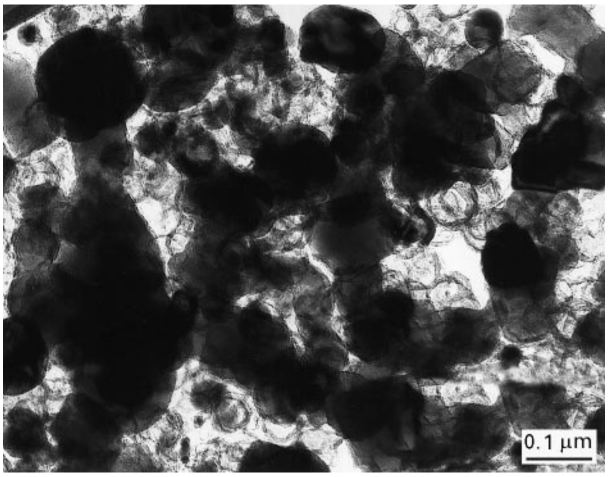

Figure 17 TEM micrograph of TiO_2 mixed with carbon black reaction product at 1300 °C for 2 h in flowing argon.

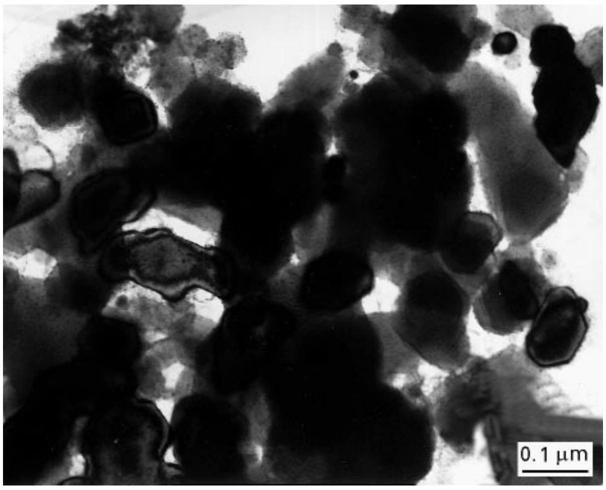

Figure 18 TEM micrograph of TiO_2 mixed with carbon black reaction product at 1400 °C for 2 h in flowing argon.

range in size from 0.01 μm (unreacted carbon) to 0.3 μm (agglomerates). Fig. 17 is a TEM micrograph of the reaction products from TiO_2 powder mixed with carbon black and reacted at 1300 °C for 2 h. The particles shown in the micrograph vary in size and show moderate agglomeration. Some particles are sintered together and are not equiaxed. The particles are in the form of TiC_xO_y and unreacted carbon at this stage of the reaction. The XRD results in Fig. 9 show that TiC_xO_y peaks are the only peaks present. A wide size distribution can be seen ranging in size from 0.01 μm (unreacted carbon) to 0.1 μm (TiC_xO_y). Fig. 18 is a TEM micrograph of the reaction products from TiO_2 powder mixed with carbon black and reacted at 1400 °C for 2 h. A small amount of free carbon is still present as the reaction nears completion. The amount of agglomeration has increased due to the lack of a consistent carbon source. The shape of the particles has also changed as the particles bond together. A wide size distribution can be seen, with particles ranging in size from 0.01 μm to 0.2 μm (TiC_xO_y). Fig. 19 is a TEM micrograph of reaction products from TiO_2 powder mixed with carbon black and reacted at 1500 °C for 2 h. Free carbon is still present, even though the reaction has completed. The XRD results in Fig. 9 confirm that a fairly pure TiC product has been formed. The particles are agglomerated and are no longer round in shape. Particles range in size from 0.1 μm to 0.5 μm (agglomerates). The mixed powder contained unreacted carbon and oxides of titanium as a result of inconsistent mixing

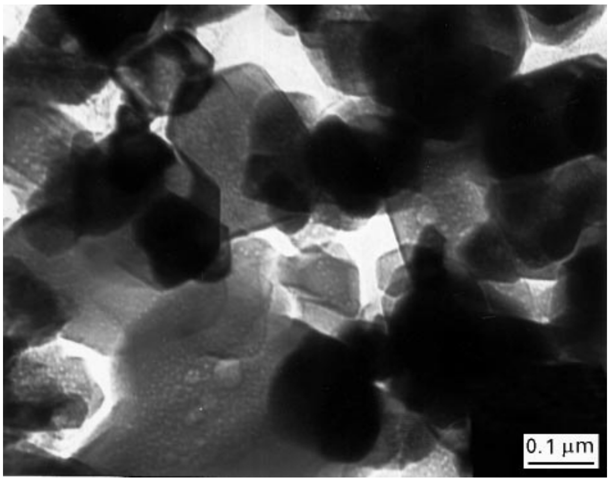

Figure 19 TEM micrograph of TiO_2 mixed with carbon black reaction product at 1500 °C for 2 h in flowing argon.

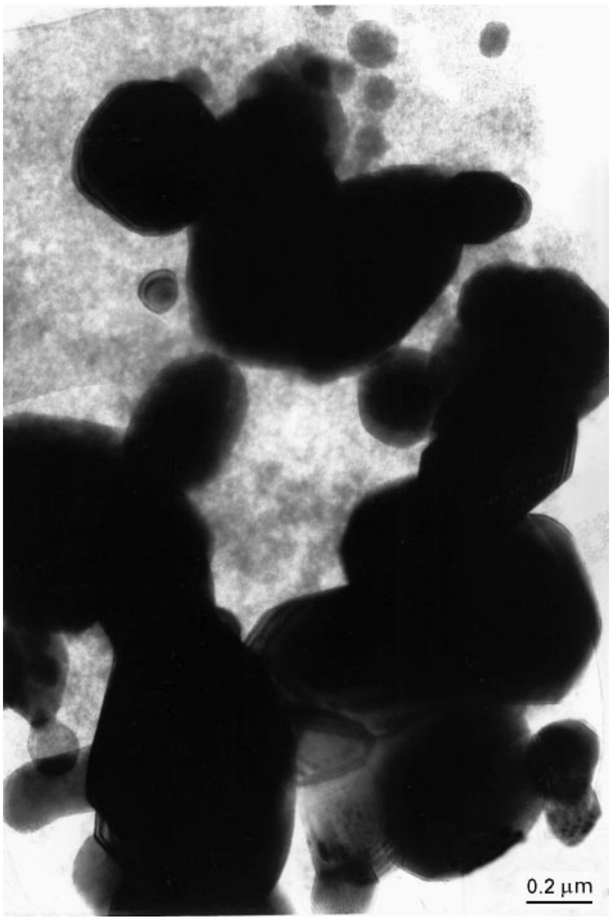

Figure 20 TEM micrograph of TiO_2 mixed with carbon black reaction product at 1550 °C for 4 h in flowing argon.

between the two. There is agglomeration present in both powders, but there is less in the coated powder and they appear to be soft agglomerates and not hard as with the mixed powder.

Fig. 20 shows a TEM micrograph of synthesized TiC powders from the mixed precursors at 1550 °C for 4 h. The synthesized TiC powders have submicron particles, oxygen content of 0.9 wt % and moderate agglomeration.

Oxygen and total carbon content were evaluated to check the purity of the powders. Fig. 21 shows the oxygen content in the produced TiC powders as a function of reaction temperature. The TiC powders were synthesized, from precursors containing 33.7 wt% carbon, at 1200–1500 °C for two hours in 1 l min^{-1} of flowing argon. The oxygen content decreased with temperature, with the mixed powder having more oxygen than the coated powders. The higher oxygen content of the mixed powders at 1200 °C confirms that there are more lower oxides present, as previously shown by the XRD patterns in Figs 8 and 9. The coated powders at 1200 °C have a much lower oxygen content, proving that the coated powders start to reduce earlier and more effectively. At 1300 to 1400 °C, the mixed powders show a lower oxygen content as reduction takes place at a higher temperature. At 1400 and 1500 °C, the oxygen contents are similar, as the reduction reactions near completion. The products at 1500 °C had a very low oxygen content, with the mixed TiO_2 having 2.3 wt%, and the coated TiO_2 having 2.2 wt%. Fig. 22 shows the total carbon content in the produced TiC powders as a function of reaction temperature. The profile of the oxygen content is similar to that shown in the total

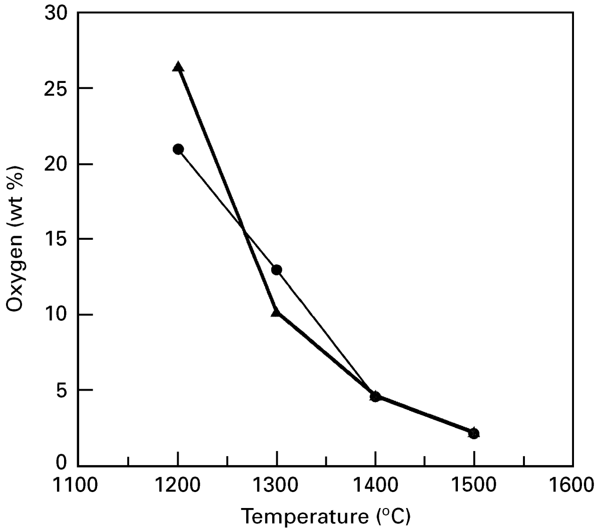

Figure 21 Oxygen content versus temperature for coated (●) and mixed (▲) TiO_2 reaction products.

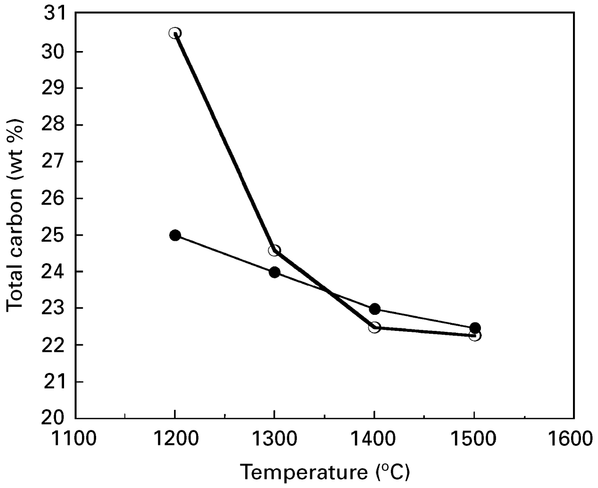

Figure 22 Total carbon content versus temperature for coated (●) and mixed (○) TiO_2 reaction products.

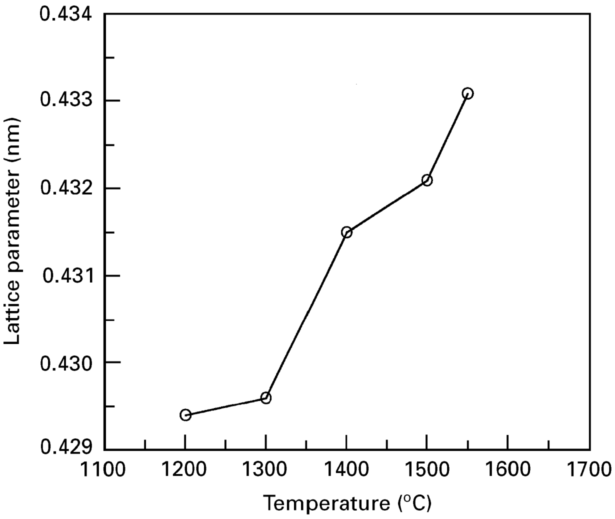

Figure 23 Lattice parameter of coated TiO_2 reaction products at 1200 to 1550 °C.

carbon content. The coated powders at 1200 °C have a much lower total carbon content than the mixed powders. The mixed powders show a lower total carbon content, as reduction takes place at a higher temperature. The products at 1500 °C have a low total carbon content which confirms a pure TiC is being produced since little free carbon was seen in the TEM (Fig. 14). There is still some free carbon present in the powders because the initial carbon content (33.7 wt %) was slightly higher than theoretical (31.08 wt %). The coated powders show a linear decrease in total carbon which suggest that carbon is being used as needed in the reduction reaction. Due to the lack of a carbon source at lower temperatures, the mixed powders consume more carbon at higher temperatures where it is more thermodynamically favourable.

As can be seen in Fig. 23, the lattice parameter increases with reaction temperature, while oxygen content decreases. Since oxygen and nitrogen are common impurities in TiC (up to as much as 50 at %) they are known to lower the lattice parameter of TiC [11]. The observed low lattice parameters of the reaction products with high oxygen content (at $1300 \sim 1400$ °C) are from TiC ($a_0 = 0.4331$ [12] or 0.4328 nm [11]) forming a solid solution with TiO ($a_0 = 0.418$ nm [13]). Fig. 23 implies that TiC_xO_y (instead of pure TiC) forms at lower temperature and then it is purified towards TiC at higher temperatures.

4. Conclusions

1. The carbon coating process was capable of producing high quality powders suitable for making ceramic materials and composites.

2. The carbothermal synthesis of titania proceeded via forming titanium oxycarbide, followed by the purification of titanium oxycarbide towards pure titanium carbide.

3. The formation of titanium oxycarbide proceeded by two routes:

(i) The uniformly coated pyrolytic carbon on fine titania particles formed a vitreous surface phase by an interaction with titania and then TiC_xO_y phase formed first from the vitreous phase. Then an additional titanium oxycarbide started to form from the residual TiO_2 via Ti_3O_5 phase. Ti_3O_5 was the oxide phase with the lowest oxidation state, before forming the oxycarbide phase in addition to the formation of TiC_xO_y.

(ii) The mixed powders first lowered their oxidation state to Ti_3O_5, followed by further reduction to Ti_2O_3. The titanium oxycarbide grew from Ti_2O_3 followed by the purification towards TiC.

4. When reacted at 1550 °C for 4 h in a flowing argon atmosphere, the carbon-coated titania resulted in titanium carbide product powders that showed:

(i) fine particle size (0.1–0.3 μm);
(ii) oxygen content of 0.6 wt%;
(iii) lattice parameter of 0.4331 nm;
(iv) uniform particle shape;
(v) loose agglomeration between particles.

5. The mixed titania and carbon black resultant titanium carbide powders synthesized at 1550 °C for 4 h in a flowing argon atmosphere showed:

(i) fine particle size (0.1–0.5 μm);
(ii) oxygen content of 0.9 wt%;
(iii) lattice parameter of 0.4328 nm;
(iv) moderate agglomeration.

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