Synthesis of TiC-TiB₂ composite powders from carbon coated TiO₂ precursors

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Abstract

Submicron TiC-TiB₂ composite powders were synthesized by carbo/borothermal reductions from a novel carbon coated TiO₂ precursors method. Reactants were also mechanically mixed for comparison. Precursors and conventionally mixed powders were reacted from 1100 to 1500°C for 2 hours in flowing argon at 1L/min. Phase evolution, thermodynamic analysis, microstructures, and surface areas were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and Brunauer-Emmett-Teller (BET) surface area analyzer, respectively. Products synthesized from precursors had high purity of TiC-TiB₂ mixture, fine particle size, narrow size distribution, regular shape, loose agglomeration, and high surface area. Powders with different compositions were also prepared by controlling the ratio between reactants. The sintering tests demonstrated that produced powders can be sintered to a 99.6% relative density using 5 wt. % nickel additives at 1550°C for 2 hours in flowing argon atmosphere.

Keywords: carbon coated precursors; TiC; TiB₂; carbothermal reduction; borothermal reduction

1. Introduction

Both titanium carbide(TiC) and titanium diboride(TiB₂) combine the advantages of high melting points, good mechanical properties, high electrical conductivities, and high resistance to oxidation and corrosion. These materials have many potential applications in key technologies from mechanical and chemical industries to electronics [1,2]. Compared with monolithic TiC or TiB₂, TiC-TiB₂ composites appear to have better properties, including high thermal shock resistance, stability under high temperature, and high fracture toughness [1]. The most

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widely studied methods to synthesize TiC-TiB₂ composite powders are self-propagating high-temperature synthesis (SHS) [3,4] and high energy ball milling [5,6,7]. Utilizing titanium, B₄C/B, and carbon as starting materials, reactions are as following:

However, very fine titanium and boron powders are needed in order to prepare high quality powders. On the other hand, large scale production is also not possible for either method. At the same time, substoichiometric TiC_x (x is smaller than 1) may also form in final products [4]. It has been demonstrated a deleterious effect on both mechanical and electrical properties [8,9]. In reaction 1, the content of TiB₂ cannot be higher than 66.7 mol. %, which means non-controllable composition. Former research has shown that fine microstructure ceramic materials have an advantage in mechanical properties [7]. Although submicron or nano size TiC-TiB₂ composite powders can be synthesized through high energy ball milling or SHS methods, long period experiment (up to 72 hours) [6,10] and annealing are required [4,6,10].

Commercial methods, which mean large scale of products and less costs, to produce TiC [11] and TiB₂ [2] are carbothermal and borothermal reduction, respectively. Mixtures of TiO₂, carbon, and B₄C are reacted at temperature up to 1800°C in a vacuum or with inert atmosphere protecting:

Compared with SHS and the high energy ball milling method, carbothermal and borothermal reduction methods are more cost effective. However, the quality of produced powders through carbothermal and borothermal reduction methods from traditional mixtures of reactants are not acceptable due to agglomeration and high level of impurities [2, 11]. In order to improve the quality of produced powders, a precursors method was developed using carbon

coated TiO_2 [12]. Instead of carbon black, the carbon is from the pyrolysis of propylene. This can eliminate the contaminations like iron, copper and other inorganic elements in carbon black. Meanwhile, pyrolysis resulted carbon deposit on the surface of TiO_2 to ensure the intimate contact between reactants. This can reduce the reaction temperature from $\sim 1800^\circ\text{C}$ to $\sim 1500^\circ\text{C}$ [11]. The produced powders also have the advantages of pure and single phase, submicron in particle size, narrow distribution, loose agglomeration, and spherical particle shape. The carbon coating precursors method has been applied in the synthesis of other powders such as TiB_2 [13], SiC [14], W [15], WC [16], CaB_6 [17], and $\text{TiC-Al}_2\text{O}_3$ [18].

The present paper aims to prepare high quality, varying compositions of TiC-TiB_2 composite powders using carbo/borothermal reduction from carbon coated precursors. The reaction equation is designed as:

Based on reaction 6, powders with different compositions will be prepared. Phase evolutions and reaction paths will be investigated and determined by both XRD results and thermodynamic analysis. Microstructures of prepared samples will also be observed. Sintering tests will be conducted to evaluate the sintering properties of synthesized composite powders.

2. Experiment

The synthesis process consists of two steps. The first step is the coating of TiO_2 (Aeroxide P25, Acros Organic, NJ) with carbon by decomposing a hydrocarbon gas (C_3H_6) at a temperature of 600°C . This step was performed in a rotating chamber furnace consisting of a 10 cm ID by 35 cm stainless steel cylinder. Approximately 100 grams of TiO_2 powders were placed in the vessel. The vessel was evacuated, purged with argon, and evacuated again. The vessel was then heated to 600°C and filled with propylene gas until the pressure reached about 3 atm. After 5 minutes, the remaining gas was released. Approximately, 1.5 grams of carbon could be deposited for each cycle. The vessel was filled with fresh propylene again to run the next cycle. The step was repeated until the desired amount of carbon was deposited. Detailed procedure of the coating process was described elsewhere [11]. The weight percentage of the carbon in the precursors is determined using thermogravimetric analysis in the air. In order to synthesize 40 wt. % TiC -60 wt. % TiB_2 composite powders, reaction 6 becomes:

Based on reaction 7, 24.4 wt. % coated carbon in the precursors is desired. The precursors were then mixed with B₄C (Grade HS, H.C Strack, Munich, German) in a plastic bottle with two methacrylate balls using a SPEX 8000 Mixer/Mill (SPEX Corp., Metuchen, NJ) for 20 minutes. In order to evaluate phase evolution, final mixtures were heated at temperatures ranging from 1100 to 1500°C for 2 hours in a tube furnace (CTF 17/75/300, Carbolite, Sheffield, UK) with flowing argon gas (1L/min). Weights of samples before and after the reaction were recorded to calculate the weight loss. Conventional mixing of TiO₂, carbon black (Monarch 880, Cabot, Boston, MA) and B₄C were prepared by the mechanically mixed method performed by the SPEX Mixer/Mill. Mixtures were also heat treated ranging from 1100 to 1500°C for 2 hours as a comparison. Microstructures of both carbon coated precursors and conventional mixtures were observed under TEM (JEM-2100F, JEOL Ltd., Tokyo, Japan). About 15 mg of each mixture was applied for differential scanning calorimetry (DSC, 404C, Netzsch, German) characterization from room temperature to 1450°C with a ramp rate of 20°C/min in flowing argon.

60 wt. % TiC-40 wt. % TiB₂ and 20 wt. % TiC-80 wt. % TiB₂ composite powders were also synthesized from carbon coated precursors. Based on reaction 6, coated carbon amount was determined as 26.9 and 21.6 wt. % respectively. The weight percentage of coated carbon was controlled by cycles of the coating process. Initial TiO₂ weight, cycles of coating process, weight percentages of coated carbon, and desired content of TiC-TiB₂ composite powders were summarized in Table 1. Carbon coated precursors were then mixed with stoichiometric amounts of B₄C and reacted at 1500°C for 2 hours with argon flowing.

Produced powders were characterized by XRD (Rigaku D/Max-B, Tokyo, Japan) using Cu K α (λ = 1.54056 Å) radiation at a voltage of 30KV and a current of 15 mA, BET gas adsorption surface area analyzer (Micromeritics, Gemini 2360, Nocrass, GA), and TEM. Phases were identified through Jade software with the International Center of Diffraction Data (ICDD). Mass fractions of produced samples were calculated based on the relative intensity of the strongest diffraction peak using the K value method [19]:

$$x_j = \frac{1}{1 + I_R K_C^J / I_j K_C^R}$$

Where x_j is j phase's mass fraction, I_j and I_R are the relative intensities of j and R phases' strongest diffraction peaks respectively, and K_C^j and K_C^R are the reference spectral intensities of j phase and R phase, respectively. Crystallite size was calculated from Scherrer equation [20]:

$$D = \frac{0.93 \times \lambda}{\beta \times \cos\theta}$$

Where D is the crystallite size, λ is the X-ray wavelength ($\lambda=1.54056\text{\AA}$), β is the line broadening at the half the maximum intensity, and θ is the Bragg angle. TiC crystallite size was estimated based on the average values from (111)(200) (220) peaks and TiB₂ from (001)(100)(101) respectively. Thermodynamic analysis and evaluations are calculated from HSC 5.1(Outokumpu Oy, Pori, Finland)

For sintering test; synthesized 40 wt. % TiC-60 wt. % TiB₂ powders from carbon coated precursors with 5 wt. % nickel powders (<1 μm , 99.5% pure, CERAC, Milwaukee, WI) were mixed in a plastics vial together with two plastics balls for 1 hour using the SPEX 8000 Mixer/Mill. Pellets were made in a single action, uniaxial press in a hardened steel die (ID=12.95 mm) under a pressure of 150MPa. The sintering process was conducted at 1550 °C for 2 hours in the tube furnace under flowing argon. Densities of sintered pellets were determined by Archimedes' method. A scanning electron microscope (SEM, FEI Quanta FEG450, Hillsboro, OR) was used to investigate the polished surfaces. Vickers hardness values were measured 10 times for the sample with Shimadzu HSV-20 hardness tester using a load of 20 kg. The fracture toughness was determined using the Vickers hardness indentation method.

3. Results and discussion

3.1. Carbon coated precursors and conventional mixtures

TEM micrographs of carbon coated TiO₂ precursors with B₄C and mechanically mixed TiO₂, carbon black, and B₄C are shown in Fig 1(a) and (b) respectively. As shown in Fig 1a, very uniform pyrolytic carbon layers are deposited on the surface of nano TiO₂ particles. This ensures the intimate contact between TiO₂ and C. Because of B₄C's submicron size, reactants can be divided into two different areas: (1) B₄C rich regions along with TiO₂ and C for the formation of TiB₂; (2) TiO₂ and C regions for the formation of TiC. Benefiting from the advantages of carbon coated precursors, sufficient and continuous carbon appears for both areas. In addition, carbon layers can

inhibit the agglomeration of produced particles and reduce the particle size[11]. While in Fig 1b, reactants just mix together and no intimate contact can be observed. No continuous carbon sources can be supplied. It also should be noticed that TiO_2 directly contacts B_4C . This may change the reaction path. The influence of powder processing methods on reaction paths will be discussed later.

3.2. DSC

DSC curves of samples from two different preparation methods are shown in Fig 2. Both curves have two endothermic peaks. Peaks for carbon coated precursors are at 1236 and 1331°C respectively. For conventional mixing samples, peaks are at higher temperatures which are 1311 and 1377°C. Compared with conventional mixing samples, carbon coated precursors show higher reactivity for the formations of both TiC and TiB_2 . Previous research shows that carbon coated precursors have higher carbothermal reductions activity[21]. At the same time, reactivity of borothermal reductions can also be improved by using carbon coated precursors. There is no extra peaks for the conventional mixing sample, although it was supposed to have more reactions because of the direct contact made between TiO_2 and B_4C . This is probably because reactions happened at similar temperature range and can not form obvious split reaction peaks.

3.3. Weight loss and phases evolutions

In carbo/borothermal reduction reactions, by comparing the actual and theoretical weight loss, fractions of the reaction can be determined. Based on reaction 7, the theoretical weight loss is 46.2%. Weight loss at each reaction temperature for different sample processing methods are shown in Fig 3. When the reaction temperature is 1100°C, neither sample shows obvious weight loss. When temperature goes up to 1200°C, carbon coated precursors samples start losing weight. Conventional mixed samples have lower weight loss. Samples from precursors reach near theoretical weight loss at 1400°C. As a comparison, the conventional mixed samples attain close theoretical weight loss at 1500°C. This is consistent with DSC results and also illustrates carbon coated precursors' high reactivity. It also should be noticed that weight loss of carbon coated precursors is close to linear between 1100 and 1400°C, while there is a slope for mixing samples between 1300 and 1400°C.

XRD patterns in Fig 4 and 5 show phases evolutions at temperatures ranging from 1100 to 1500°C. For the carbon coated precursors method, phases are identified to be Ti_3O_5 , B_2O_3 and TiC_xO_y at 1100°C. B_2O_3 , TiC_xO_y , and TiB_2 phases appear at both 1200 and 1300°C. Intensities of B_2O_3 peaks decrease and TiB_2 increase between 1200 and 1300°C. Sharp TiC and TiB_2 peaks form at 1400°C and 1500°C with no other impurity, which means pure phases TiC- TiB_2 composite powders are synthesized. For conventional mixed samples, more complicated reactions happened. Phases from carbon mixing method are determined to be TiBO_3 , Ti_2O_3 , Ti_3O_5 , and B_2O_3 at 1100°C; TiBO_3 , Ti_2O_3 , B_2O_3 , and TiC_xO_y at 1200 °C; TiBO_3 , B_2O_3 , and TiC_xO_y at 1300 °C; B_2O_3 , TiB_2 , and TiC_xO_y at 1400 °C. Sharp TiC and TiB_2 peaks can be observed until 1500°C. It should be clarified that TiC_xO_y and TiC were identified based on their lattice parameters. It is well known that TiC_xO_y has a smaller lattice parameter than TiC[11]. For this current paper, if the lattice parameter was smaller than 4.327Å (ICDD card 32-1383, TiC), the phase was identified as TiC_xO_y ; otherwise, TiC was determined. Phases in evolutions and strength are also summarized in Table 2. Based on the XRD patterns in Fig 4e and 5e, the calculated TiB_2 mass fraction for carbon coated precursors is 59 wt. %, comparing with 55 wt. % for the mechanically mixing method.

Surface areas of samples from different preparation methods are shown in Fig 6. Both values increase at low temperature range. While reaction continues, surface areas decrease as a result of carbon eliminating. Finally, the sample at 1500°C from precursors has a surface area of 5.8 m²/g, comparing with 10.7 m²/g from mixed samples. It is hypothesized that the mixed samples contain a significant amount of unreacted carbon black and lead to the high surface area.

3.4 Reaction paths and thermodynamic analysis

Based on discussions about XRD patterns as shown in Fig 4 and Fig 5, there are five main differences between two processing methods. (1) The lowest oxide form for precursors samples is Ti_3O_5 contrasting Ti_2O_3 for conventional mixed samples. (2) TiC_xO_y forms at 1100°C for precursors samples comparing with 1200°C for conventional mixed samples. (3) The weight percentage of TiB_2 calculated from XRD patterns (Fig 4e, carbon coated precursors, and Fig 5e, conventional mixed samples) is 59 wt. % and 55 wt. % respectively. (4) TiB_2 start forming at 1200°C (Fig 4b) from carbon coated precursors samples. As a comparison, TiB_2 peaks show up at 1400°C for mixed samples. (5) TiBO_3 phase can be identified for mixed sample at temperatures ranging between

1100 and 1300°C, which does not appear for carbon coated precursors. In order to understand the reasons of those differences, it is necessary to analyze the reaction paths. This also helps find out how those differences can influence the reaction routes.

Previous research studies the reaction paths toward TiC [11]. The carbothermal reduction of TiO₂ to its oxide happens at 1100°C for both methods[11,21]:

For carbon coated precursors samples, continuous and sufficient carbon sources ensure the high reactivity. Ti₃O₅ reacts with carbon and reduces to TiC_xO_y at 1100°C:

Ti₃O₅ is the lowest oxide form instead of Ti₂O₃ in carbon coated precursors [11].

For mixed samples, there is one more reaction: Ti₃O₅ reduces to Ti₂O₃ because of insufficient carbon source. Ti₂O₃ then reacts with carbon to form TiC_xO_y at 1200°C [11]:

The favorable reaction temperature for reaction 10 is 1371°C. It is higher than the favorable temperatures for the formations of TiC from TiO₂, Ti₂O₃, and Ti₃O₅. Although flowing argon can reduce the partial pressure and cause the reaction to be favorable at 1100°C, the high favorable temperature still prevent the whole reaction. Above discussions show the reasons of differences (1) and (2).

Reaction paths of borothermal reductions are not clear yet. Usually, it is believed that TiO₂ reacts with carbon and B₄C to form TiB₂ and B₂O₃[22]:

With temperature increased to 1112°C, the reaction between TiO₂, C, and B₄C becomes favorable:

Gibbs free energy, ΔG , as a function of reaction temperature for reaction 13 at atmosphere pressure is shown in Fig 7. It is known that B₂O₃ has a melting point of 465°C and may evaporate at reaction temperature range. Vaporization of B₂O₃ leads to excess TiC in final powders. This is same with the formation of ZrB₂ which has been discussed in Guo's report. 25 wt. % excess B₄C is added in order to have single phase ZrB₂[23]. The requirement of reaction 13 is sufficient carbon sources. Carbon coated precursors have sufficient and continuous carbon sources. This is the reason that TiB₂ forms at 1200°C for carbon coated precursors (Fig 4b). Relative low favorable temperature of reaction 13 also minimize the vaporization of B₂O₃ and ensure the weight percentage of TiB₂ (59 wt. %) matches the theoretical value (60 wt. %).

As discussed in TEM microstructures of conventional mixed samples (Fig 1b), TiO₂ directly touch with B₄C and lead to the formation of TiBO₃ (Fig 5 a-c):

This has been observed in previous research in which TiO₂ is contacting B₄C [24]. Reaction 14 can also happen where there is insufficient carbon source. For conventional mixed samples, it can not make sure there are sufficient and continuous carbon sources. Reaction 14 is more favorable. As shown in Fig 5, because of the existence of TiBO₃, TiB₂ peaks can not be identified until 1400°C. When temperature reaches 1400°C, TiO₂, TiC, Ti₃O₅, and Ti₂O₃ may react with B₂O₃:

As shown in Fig 7, favorable reaction temperatures for reactions 16-19 are 1374°C, 1438°C, 1400°C, and 1399°C respectively. This gives an explanation for the formation of TiB_2 at 1400°C in conventional mixed samples. Fig 7 shows the different formation temperatures of TiB_2 from different sample processing methods. Also, considering the high reaction temperature, B_2O_3 can vaporize at a higher rate. As shown in Fig 3, the extreme change between 1300 and 1400°C also demonstrates the vaporization of B_2O_3 . Deficiencies of boron sources then leads to the lower weight percentage of TiB_2 in synthesized composite powders (55 wt. %).

3.4. TEM micrographs of final products

TEM micrographs of produced powders from carbon coated precursors are shown in Fig 8. TiB_2 particles have a particle size from 0.7 to 0.9 μm . Fine TiC particles ranging from 0.1 to 0.2 μm with narrow size distribution can be seen. All particles are loosely agglomerated, however, a few neck growths can be observed. Trace free carbon can be observed through TEM. Diffraction patterns of selected single particles confirm the formation of TiC and TiB_2 . Micrographs of samples made from conventional mixing methods are shown in Fig 9. Although fine TiB_2 and TiC particles with regular shape can also be observed, there are still some unknown particles. These might be the intermediate phases such as TiBO_3 and B_2O_3 . At the same time, a certain amount of unreacted carbon black is still left in the sample as shown in Fig 9 (b). TEM micrographs confirm former results about XRD patterns and BET surface areas. Reaction is not completed at 1500°C for samples from conventional mixing. Carbon coated precursors show high reactivity because of intimate contact and continuous carbon sources. Sample made from carbon coating precursors at 1500°C features fine particle size and shape, high purity, and loose agglomeration.

3.5. Controlling of composition

Another two batches powders with compositions of 60 wt. % TiC -40 wt. % TiB_2 and 20 wt. % TiC -80 wt. % TiB_2 , were synthesized at 1500°C for 2 hours under flowing argon. Their XRD patterns along with 60 wt. % TiB_2 samples are shown in Fig 10. Similar with former results and discussion, there is no extra containment phase. Sharp and strong TiC and TiB_2 peaks can be observed. BET surface areas, calculated mass fractions and crystallite sizes from XRD patterns of produced powders are shown in Table 3. Mass fractions shown TiC - TiB_2 composite powders with variable composition can be controlled by changing the ratio of TiO_2 , carbon and B_4C . Weight percentages of TiB_2 are matching with theoretical values. As discussed before, reaction 13 dominates the formation route of TiB_2

and minimizes the vaporization of B_2O_3 . Calculated crystallite size is approximately 30 to 50 nm for each component. Values are comparable with samples from 4 to 8 hours high energy milled [7]. Surface areas are related with composite compositions. This is because TiC has smaller particle size which means higher surface area.

3.6. Sintering and mechanical properties

One of the most important applications of TiC-TiB₂ composites is as cutting tool materials. With 5 to 25 wt.% Ni as a binder, sintered samples show outstanding hardness and fracture toughness [25,26,27]. In order to evaluate the sintering properties of produced powders with nickel additive, sintering studies were performed on the synthesized composite powders with content of 40 wt. % TiC-60 wt. % TiB₂. By adding 5 wt. % nickel, samples are sintered to a relative density of 99.6% through pressureless sintering (PS) at 1550°C for 2 hours in flowing argon. A backscattered detector (BSD) micrograph of the polished surface is shown in Fig 11. Gray TiC grains and dark gray TiB₂ grains are embedded in nickel binder. The Vickers hardness is 24.7 ± 0.6 GPa based on 10 times examinations. Fracture toughness was calculated by measuring the crack lengths using the equation derived by Anstis[28]. Fracture toughness is $7.5 \pm 1.5 \text{ MPa} \cdot \text{m}^{1/2}$ from calculation.

From previous reports, Ogburn claims that commercial TiC and TiB₂ mixtures can be sintered with 5 wt. % Ni + X at 1550°C and have a ~85% relative density[29]. In order to reach high relative density(above 95%), a sintering temperature of 1650°C with applied external pressure is needed. Both Zou and Huang report a sintering temperature of 1650°C through hot pressing to prepare dense TiC-TiB₂-Ni cermet[25,26]. The Vickers hardness are between 22.54 and 23.5 GPa with fracture toughness ranging from 7.5 to $7.8 \text{ MPa} \cdot \text{m}^{1/2}$. For current research, a sintering temperature of 1550°C through PS leads TiC-TiB₂-Ni cermet to a high relative density. PS at relative low temperature greatly improves the production efficiency. At the same time, sintered composites show an outstanding combination of high hardness and toughness.

4. Conclusion

Submicron TiC-TiB₂ composite powders, with TiC particle size about 0.1 to 0.2 μm and TiB₂ about 0.7 to 0.9 μm , were synthesized by carbo/borothermal reduction from carbon coated TiO₂ precursors at a relative low temperature(1500°C for 2 hours). Final products combine the advantages of pure phases, fine particle size, narrow

size distribution, loose agglomeration, and high surface area. Compositions of the powders can be controlled by changing the ratio between TiO₂, carbon and B₄C. Produced powders with 5 wt.% nickel can be sintered to a 99.6% relative density with outstanding Vickers hardness (24.7 ± 0.6 GPa @20kg) and fracture toughness (7.5 ± 1.5 MPa*m^{1/2}).

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Table 1 Summary of initial weight of TiO₂, cycles of coating process, weight percentages of coated carbon, and desired content of TiC-TiB₂ composite powders

Initial weight of TiO ₂	Cycles of coating process	Weight percentage of coated carbon	Desired content of TiC-TiB ₂ composite powders
100 grams	25	26.9 wt %	40 wt%TiB ₂ -60 wt % TiC
100 grams	21	24.4 wt %	60 wt%TiB ₂ -40 wt % TiC
100 grams	18	21.6 wt %	80 wt%TiB ₂ -20 wt % TiC

Table 2 Summary of phases and their strength from different sample preparation methods and temperatures from XRD*

Sample preparation method	Reaction temperature	TiBO ₃	Ti ₂ O ₃	Ti ₃ O ₅	B ₂ O ₃	TiC _x O _y	TiC	TiB ₂
Carbon coated precursor	1100°C	N	N	VW	M	M	N	N
	1200°C	N	N	N	M	S	N	VW
	1300°C	N	N	N	W	S	N	M
	1400°C	N	N	N	N	N	VS	VS
	1500°C	N	N	N	N	N	VS	VS
Conventional mixing	1100°C	VS	VW	M	W	N	N	N
	1200°C	S	VW	N	W	M	N	N
	1300°C	VW	N	N	W	S	N	N
	1400°C	N	N	N	VW	S	N	W
	1500°C	N	N	N	N	N	VS	VS

W: weak; N: none; M: medium; VW: very weak; S: strong; VS: very strong

*Holding time is two hours for each sample

Table 3 Summary of mass fraction and crystallite size of synthesized TiC-TiB₂ composite powders

Theoretical composition	Mass fraction	TiC crystallite size	TiB ₂ crystallite size	Surface area
40 wt%TiB ₂ -60 wt % TiC	39 wt % TiB ₂	42±3 nm	47±3 nm	7.2 m ² /g
60 wt%TiB ₂ -40 wt % TiC	59 wt % TiB ₂	40±2 nm	47±1 nm	5.8 m ² /g
80 wt%TiB ₂ -20 wt % TiC	78 wt % TiB ₂	31±5nm	39±2 nm	4.7 m ² /g

Fig. 1. TEM microstructures of mixtures from different sample preparation methods. (a) carbon coated precursors, (b) conventional mixed samples.

Fig. 2. DSC curves for carbon coated precursors and conventional mixing.

Fig. 3. Weight loss of sample from different preparation methods.

Fig. 4. XRD patterns for samples from carbon coated precursors at different temperature. (a) 1100°C, (b) 1200°C, (c) 1300°C, (d) 1400°C, (e) 1500°C.

Fig. 5. XRD patterns for samples from conventional mixed samples at different temperature. (a) 1100°C, (b) 1200°C, (c) 1300°C, (d) 1400°C, (e) 1500°C.

Fig. 6. BET surface area of samples from carbon coated and carbon mixed precursors as a function of reaction temperature.

Fig.7 Gibbs' free energy as a function of temperature at atmosphere pressure for reaction 13, and reactions 15-18

Fig. 8. TEM micrographs of synthesized TiC-TiB₂ composite powders from carbon coated precursors at 1500°C for 2 hours and their diffraction patterns. (a) mixtures of TiC and TiB₂, (b) enlarge view of TiC particles, (c) diffraction patterns of selected single particle TiB₂, (d) diffraction patterns of selected single particle TiC.

Fig. 9. TEM micrographs of synthesized TiC-TiB₂ composite from conventional mixing at 1500°C for 2 hours. (a)mixtures of TiC and TiB₂, (b)enlarge view of TiC particles.

Fig. 10. XRD patterns of composite powders with different compositions. (a) 40 wt. % TiB_2 and 60 wt. % TiC , (b) 60 wt. % TiB_2 and 40 wt. % TiC , (c) 80 wt. % TiB_2 and 20 wt. % TiC .

Fig. 11. A BSD micrograph of the polished surface for sample sintered with 5 wt. % nickel.