JMEPEG (2009) 18:273–277
DOI: 10.1007/s11665-008-9278-5

1059-9495/$19.00

Synthesis of B_4C-Nano TiB_2 Composite Powder by Sol-Gel Method

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(Submitted November 11, 2007; in revised form May 22, 2008)

Production of (B_4C-nano TiB_2) composite powder by chemical method was evaluated in this study. Starting materials were boron carbide, carbon, and titanium (IV) iso propoxide (TTIP). Water was used as a hydrolyser agent. TTIP was hydrolyzed with water and, consequently, amorphous $Ti(OH)_4$ was formed. Heat-treatment of $Ti(OH)_4$ at 100 and 850 °C led to the production of TiO_2 and TiB_2 phases, respectively. The effect of heat-treatment time and temperature on the phase transformation and size of the produced nano powder were investigated. The produced nano powder was characterized by XRD, SEM, and DTA. It was found that heat-treatment time and temperature have significant effects on the amount and size of the produced TiB_2 powder. The data also reveal that the minimum temperature for TiB_2 formation is 650 °C.

Keywords B_4C-nano TiB_2, boron carbide, carbon, composite powder, TTIP

1. Introduction

High hardness, heat and wear resistance, low specific weight, resistance to chemical attacks, and high cross section for neutron absorption and resistance to irradiation are the most important characteristics of B_4C. Therefore, it is an extremely promising candidate for application in wear-resistant parts, neutron-absorbing and armor materials (Ref 1-6). Due to highly covalent bonding between B and C atoms and also the associated slow diffusion rate, the pressureless sintering of B_4C is difficult (Ref 7-12).

Furthermore, its relatively low strength and fracture toughness have restricted widespread applications of B_4C. Various solutions have been studied to overcome the abovementioned obstacles. One of the most well-known techniques (solutions) is pressureless sintering of B_4C in the presence of sintering aides. However, inhomogeneous distribution of additives and high cost of these materials are the main problems of this method (Ref 8-15). In situ chemical synthesis of sintering aide is an extremely promising method to solve the abovementioned problems. The possibility of the nano composite powder production, with higher activity and therefore better sintering capability, is one of the most important advantages of this technique compared to other processing methods.

The possibility of titanium hydroxide ($Ti(OH)_4$) coating production on the surface of B_4C particles via sol-gel method was investigated in the present study. Phase transformation of $Ti(OH)_4$ to nano-TiB_2 and production of (B_4C-nano TiB_2) composite powder were also evaluated.

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2. Experimental Procedures

2.1 Starting Materials

Boron carbide powder (Chengdu Rong Feng, China) was used as the main raw material. The chemical composition and scanning electron microscope (SEM) of this powder are shown in Table 1 and Fig. 1, respectively.

Titanium (IV) iso propoxide or (TTIP) $Ti[OCH(CH_3)_2]_4$ (Alfa Aesar) with molecular weight of 284 g was also used as the source of Ti. The purity of TTIP was ~97%.

2.2 Sol-Gel Production

B_4C powder was added to ethanol and then mixed completely. Distilled water and the solution of diluted TTIP with alcohol were then added to the suspension of B_4C and ethanol. Conditions of the process are shown in Table 2. To prevent from rapid hydrolyses of TTIP, the distilled water was already diluted with iso propanol. A total of 0.015 mole of TTIP was used for 1 g of B_4C and the amount of water was triple of TTIP.

The produced solution was stirred for 6 h at room temperature using a mechanical stirrer. After stirring, the solution was dried at 140 °C to evaporate the existence solvent. Gel was formed as a result of solvent evaporation from the sole. In order to eliminate the molecular water of $Ti(OH)_4$ as well as TiB_2 coating fabrication, the produced gel was heated in a furnace under argon atmosphere. Some part of required carbon element was introduced by the graphite crucible.

2.3 Characterization of the Produced Powder

The chemical composition of the produced powders was measured by XRD (model expert, Philips). The morphology of the powders and their phase distribution were studied using SEM (Camscan MV2300).

3. Results and Discussion

Figure 2 shows the XRD patterns of the coated B_4C before and after heat treatment. The samples were heat-treated at 650,

750, and 850 °C for 1 and 3 h. The XRD pattern of untreated sample is illustrated in Fig. 2(a). As shown in the figure, only B_4C peaks can be seen in this pattern. The XRD pattern of the sample heat-treated at 550 °C is shown in Fig. 2(b). The pattern shows that B_4C-TiB_2 composite powder was synthesized as a result of reaction between B_4C and TiO_2 which has been caused by heat treatment. However, because of inadequate heat-treatment temperature, some parts of TiO_2 starting material are still present in the products. The XRD patterns of the other samples show that (B_4C-TiB_2) composition is formed in all of the specimens. The data indicate that the intensity of TiO_2 peaks (residual phase) was decreased with temperature increasing, while the intensity of the TiB_2 peaks (produced phase) was increased with temperature increasing. It can also be seen in the figures that the amount and the size of the TiB_2 nano powders were increased with heat-treatment time and temperature increasing.

Figure 2(f) shows that in the sample heated at 650 °C for 3 h, the peaks of the TiO_2 phase completely disappeared, while the peaks of the TiB_2 phase are very intensive. This can be attributed to the effect of heat-treatment time.

During powder processing, TiO_2 phase is formed from TTIP material according to the following reactions:

$$Ti[OCH(CH_3)_2]_4 + 4H_2O = Ti(OH)_4 + 4C_3H_7OH \quad \text{(Eq 1)}$$

$$Ti(OH)_4 = TiO_2 + 2H_2O \quad \text{(Eq 2)}$$

The sedimented TiO_2 is reacted with B_4C according to the reactions 3-5.

$$B_4C + TiO_2 + 3C = 2TiB_2 + 4CO$$
$$\Delta G = 89.050 \text{ kJ/mol } (627\,^{\circ}C) \quad \text{(Eq 3)}$$

$$B_4C + \frac{2x}{3+x}TiO_2 + 3C = \frac{2x}{3+x}TiB_2 + \frac{4x}{3+x}CO + \frac{3x}{3+x}B_4C_{1-x} \quad \text{(Eq 4)}$$

$$B_4C + \frac{2x}{3+x}TiO_2 + 3C = \frac{2x}{3+x}TiB_2 + \frac{2x}{3+x}CO + \frac{3x}{3+x}B_4C_{1-x} \quad \text{(Eq 5)}$$

Based on the other researchers' findings, the products of these reactions are TiB_2 and CO_2 or CO gases. Required carbon for the abovementioned reactions is supplied by B_4C, or is added directly to the starting material (Ref 13).

The patterns of thermal analysis during reaction between B_4C and TiO_2 are shown in Fig. 3.

The endothermic peak of water evaporation can be seen at 100 °C (point 1). Phase transformation of $Ti(OH)_4$ to TiO_2 is illustrated by an exothermic peak at 250 °C (point 2). Another peak can be seen at the range of 550-800 °C (point 3). Free energy evaluation (Eq 3) shows that this peak is probably associated with reaction between B_4C and TiO_2.

The SEM micrographs of the samples before and after heat-treatment are shown in Fig. 4. The micrograph of the nano powders heat-treated at 550 °C for 1 h is illustrated in Fig. 4(a). It shows that a coating consisting of $Ti(OH)_4$ nano-powder is formed on the surface of the B_4C particles. These nano powders are agglomerated on the surface of B_4C particles. The micrograph of the samples after heat-treatment at 650 °C for 1 h is demonstrated in Fig. 4(b). It shows that TiB_2 and TiO_2 powders are formed on the surface of B_4C particles. Figure 4(c) and (d) shows the image of the samples, produced at 750 and 850 °C, respectively. They show that the size and the amount of produced TiB_2 powder are increased with temperature increasing.

Table 1 Chemical composition of B_4C

Chemical composition	wt.%
B	76.1
C	20.3
B + C	96.4
B_2O_3	1.96
Fe	0.73
Si	0.91

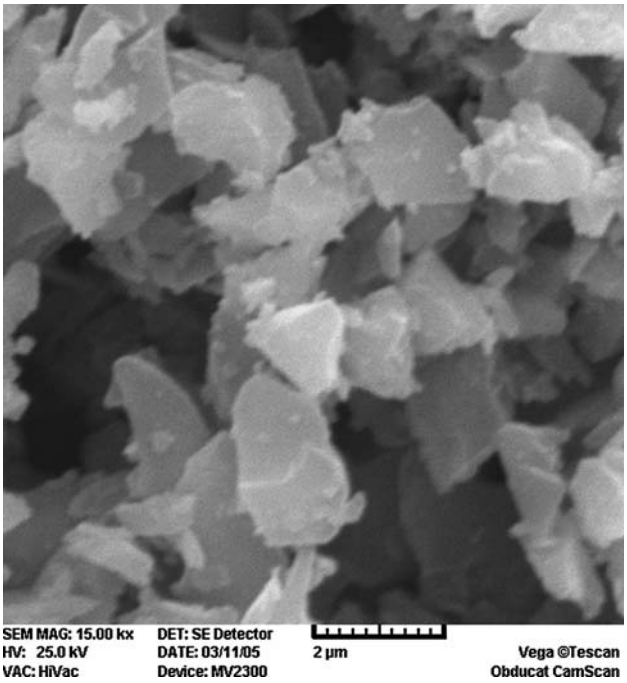

Fig. 1 SEM image of B_4C powder

Table 2 Conditions of the process

Samples	TTIP, g	Water, g	Aging, h	Isopropanol, mL	B_4C, g	Heat treatment, °C	Time, h
A	41.322	12.4	6	3000	10	650	1
B	41.322	12.4	6	3000	10	750	1
C	41.322	12.4	6	3000	10	850	1
D	41.322	12.4	6	3000	10	850	3

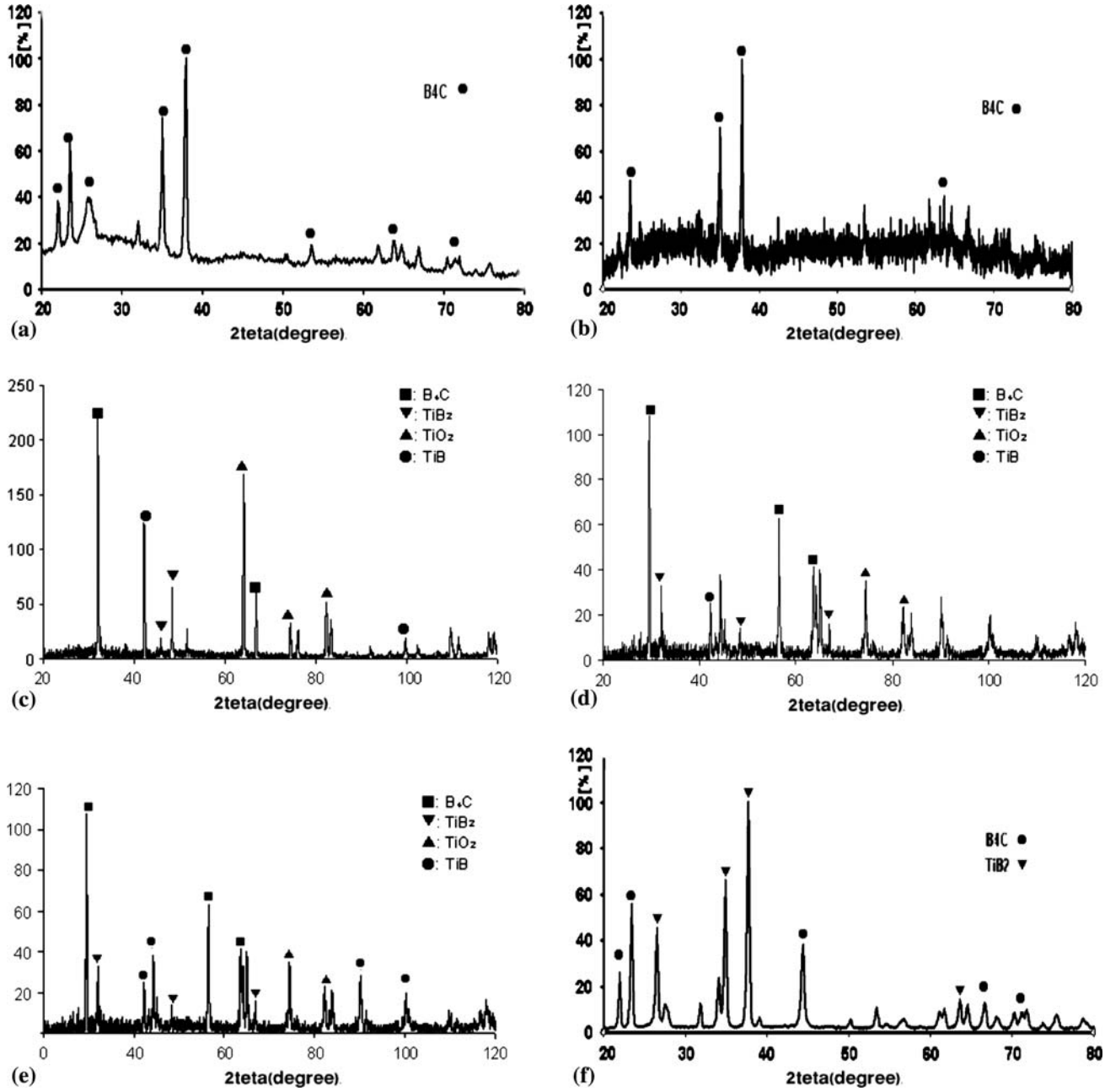

Fig. 2 XRD patterns of the coated B_4C (a) before heat-treatment and after heat-treatment at (b) 550 °C for 1 h, (c) 650 °C for 1 h, (d) 750 °C for 1 h, (e) 850 °C for 1 h, and (f) 650 °C for 3 h

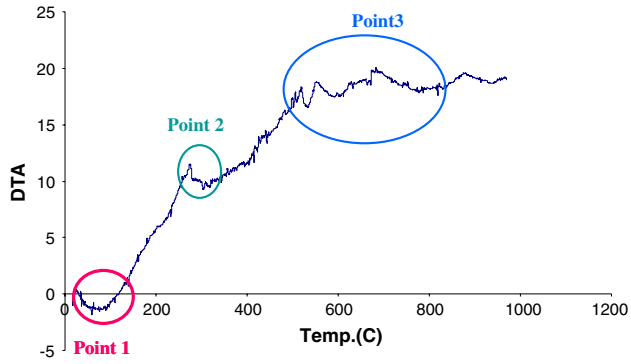

Fig. 3 The pattern of thermal analysis during reaction between B_4C and TiO_2

The effect of heat-treatment time on the SEM micrographs of the specimens is shown in Fig. 4(b), (e), and (f).

These samples were heated at 650 °C for 1-3 h. It can be seen that the size of the produced TiB_2 powders at 650 °C for 1 h is less than 50 nm (Fig. 4b). However, the size of the TiB_2 powders was increased to 100 and 200 nm with heat-treatment time increasing to 2 and 3 h, respectively (Fig. 4e and f).

4. Conclusion

1. Heat-treatment time and temperature have significant effects on the amount and the size of the produced TiB_2 powder.

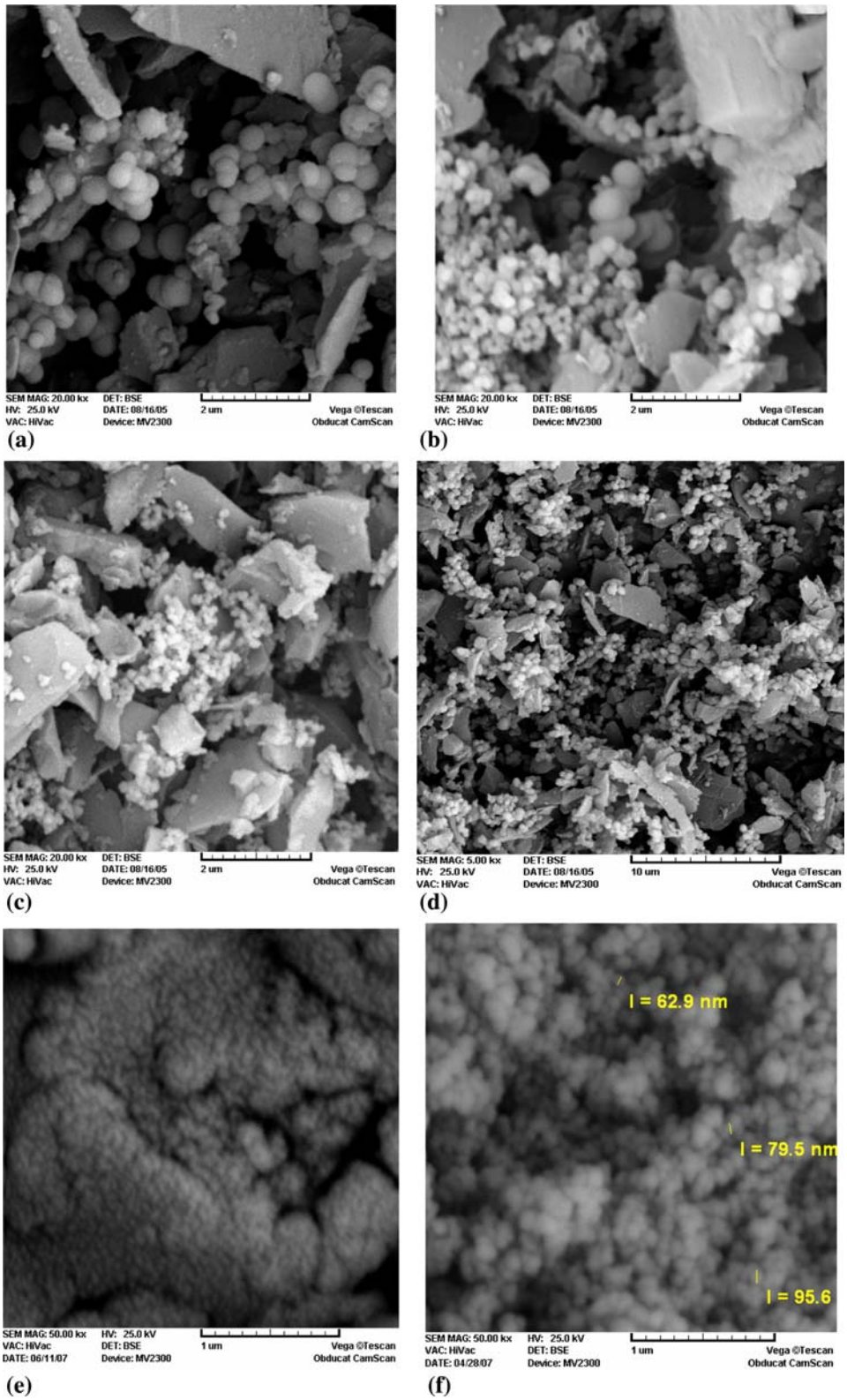

Fig. 4 SEM micrographs of the samples after heat-treatment at (a) 550 °C for 1 h, (b) 650 °C for 1 h, (c) 750 °C for 1 h, (d) 850 °C for 1 h, (e) 650 °C for 2 h, and (f) 650 °C for 3 h

2. The minimum temperature for TiB_2 fabrication is 650 °C.
3. The size and the amount of the produced TiB_2 powder are increased with temperature increasing.
4. Appropriate conditions (time and temperature) for complete phase transformation are 2 h and 650 °C.
5. TiB_2 particle size is increased from 50 to 200 nm with heat-treatment time increasing from 1 to 3 h.

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