Synthesis of B$_4$C-SiC in-Situ Composite Powders through Carbothermic Reactions

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In recent years silicon carbide (SiC) has drawn attention due to its outstanding useful physical and chemical properties such as high hardness, low density, superior chemical inertness etc. Thus, SiC is a strong candidate for several high-tech applications. Numerous attempts have been made to improve its performance. Hard ceramic particles (TiB$_2$, B$_4$C, TiC, and Al$_2$O$_3$ etc.) were added to SiC matrix to improve its mechanical properties. In the current study, B$_4$C-SiC in-situ composite powders were synthesized successfully via mechanochemical processing by using a powder mixture of B$_4$C, SiO$_2$ and black carbon. After mechanical preparation, the powder mixtures have reacted at 1400–1600 °C for various time intervals under Ar atmosphere. The resulting powders were characterized by XRD. Microstructure investigations were carried out to determine the distribution and morphology of SiC and B$_4$C grains. The XRD pattern of the yield powder reveals B$_4$C-SiC biphase composite powder. SEM images show net-shaped fibrous SiC structures and ultra-fine nanofibrous particles of 50–100 nm in diameter.

1. Introduction

Development of SiC ceramics for aerospace and nuclear industries, for bearings, mechanical seals, nozzles, turbine parts, heat exchangers, cylinder liners, a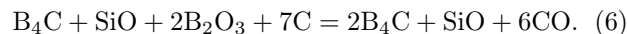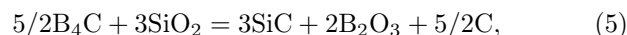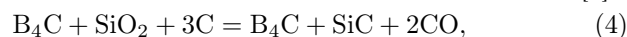nd for cutting tools have recently been in the focus of research, because of their superior properties, such as low density, high strength and toughness, high melting points, good oxidation and thermal shock resistance [1–8]. For this reason SiC can be chosen as a better candidate material by a number of researchers [9, 10].

SiC-B$_4$C composite materials have been shown to have a combination of desirable mechanical and thermal properties in recent investigations [11]. SiC-B$_4$C composite ceramics can offer a combination of high hardness and fracture toughness with a light weight. This type of hybrid ceramics can be produced by several methods, such as carbothermal reduction and carburization (CRC), mechanical alloying, spark plasma sintering and hot pressing [12].

Carbothermal reduction method can be classified as an easier and cheaper method [13–15]. Corresponding reactions are shown in Eqs. (1) and (2). With a similar method SiC can be synthesized from SiO$_2$ starting material by using carbon reducing agent though Eq. (3).

$$B_2O_3 + 7C = B_4C + 6CO, \tag{1}$$

$$4H_3BO_3 + 7C = B_4C + 6CO + 6H_2O, \tag{2}$$

$$SiO_2 + 3C = SiC + 2CO. \tag{3}$$
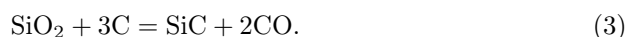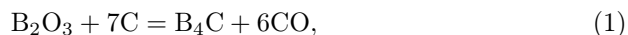
The addition of some seeding additives (B$_4$C or SiC) to the carbothermal reduction and carburization (CRC) can change transformation kinetics of reaction due to nucleation effect. The reaction (1) consist of two main reactions, given by Eqs. (5) and (6). The first one is the reaction of SiO$_2$ with B$_4$C to form SiC, B$_2$O$_3$, and C. The second is the reaction of intermediate products with C, such that all C in solid state oxides to CO above 1558 °C [8].

$$B_4C + SiO_2 + 3C = B_4C + SiC + 2CO, \tag{4}$$

$$5/2B_4C + 3SiO_2 = 3SiC + 2B_2O_3 + 5/2C, \tag{5}$$

$$B_4C + SiO + 2B_2O_3 + 7C = 2B_4C + SiO + 6CO. \tag{6}$$

In the present study, the carbothermic method has been used to synthesize silicon carbide powder from high purity silica and carbon black raw materials. In addition, effects of the B$_4$C and SiC nucleants on this reaction were investigated in detail.

2. Experimental

The purpose of the present study was to synthesize SiC/B$_4$C composite powders by using silica and carbon starting materials and the CRC method. The nucleation effect of B$_4$C and SiC on synthesis of SiC by carbothermal reactions was investigated by changing the stoichiometric ratios, and the amount and the type of seeding additive. The compositions of the samples used in the experimental procedure are shown in Table I.

SiO$_2$ used in this study was obtained from Ege Kimya Company, Turkey. Carbon black (Vulcan XC 72), which was used as the reducing agent, was received from Cabot. It had purity of 99.7% and the specific surface area of 110 m^{2}g^{-1}. Second phase component, the boron carbide, having the mean particle size of 10 μm was received from Alfa Aesar. SiC powders were used as the nucleant material.

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Compositions used in experiments (wt.%).　　　TABLE I

Exp. No.	SiO_2	C	B_4C	SiC
1	1.25	3.75	–	–
2	1.25	3.75	–	–
3	1.00	4.00	–	1.00
4	1.19	3.57	0.25	–
5	1.13	3.58	0.50	–
6	1.07	3.19	0.75	–
7	1.13	3.38	0.25	0.25
8	1.07	3.19	0.50	0.25
9	1.00	3.00	0.75	0.25
10	1.00	3.00	0.50	0.50
11	1.00	3.00	1.00	–

Silica was mixed with carbon black just above the stoichiometric ratio according to reaction (3). B_4C or SiC was added at different ratios according to Table I. Each powder mix (except exp. 1) was milled for about 24 h in a polyethylene bottle with a zirconia ball.

The CRC reactions were carried out using a tube furnace (Protherm PTF Series) under Ar (99.999 purity, Linde Group, Turkey) at 1400–1600 °C for 4 h. After the reaction, the product was heated in an ashing furnace to burn out the residual carbon in air at 900 °C for 2 h.

Powder morphology was revealed using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) was used to determine the elemental composition. The yield powders were analyzed using an X-ray diffractometer (Rigaku D/MAZ/2200/PC, Japan) with Cu K_α radiation source ($\lambda = 1.540454$ Å to identify the synthesized phases.

3. Results and discussion

Diffraction pattern in Fig. 1 belongs to the produced powders with various compositions. The results show that β-SiC, SiO_2, B_4C and amorphous phases were formed at various rates. The conversion from SiO_2 to SiC was achieved above 1500 °C with B_4C mostly staying stable.

Sample in Fig. 1a gave better results than samples in Fig. 1b and c. Minor amount of silica remained as an unreacted reactant. All samples contain amorphous phase with amount decreasing from Fig. 1c to Fig. 1a. There was obviously an increase in the amount of B_4C resulting in the increase in the amount of non-crystalline phases. The dominant phase for all compositions was SiC, having peaks with strong intensity. In this case SiC can be accepted as the matrix phase in the synthesized composite powder as was initially assumed. These results explain that the in-situ SiC-B_4C composites can be successfully synthesized with composition number 4.

SEM micrograph and elemental analysis of the SiC powders synthesized after CRC at 1450 °C for 4 h from the sample with 20 wt.% of SiC nucleant is given in Fig. 2.

Previous works have shown that synthesis temperatures under 1500 °C were not adequate for the conversion
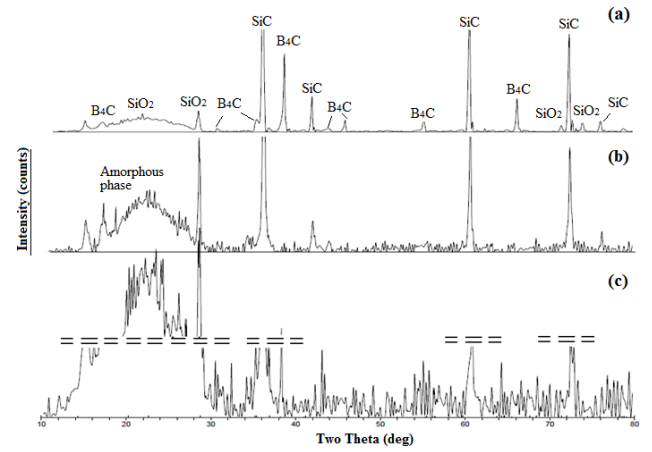

Fig. 1. X-ray diffraction patterns after synthesis of sample 4 (a), sample 7 (b) and sample 11 (c).
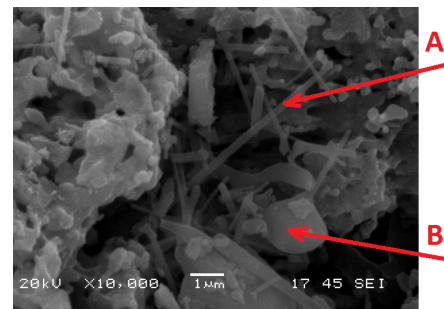

Fig. 2. SiC particles after CRC at 1450 °C for 4 h, synthesized from the sample with 20 wt.% of SiC nucleant.

of SiO_2 to SiC. SiC fibrous grains (A point in Table II) can be obviously seen in Fig. 2. In addition, unconverted SiO_2 particles (B point in Table III) can be also present. SiC, added to the starting powders, acted as seeding-agent and supported the SiC formation mechanism and the conversion.

EDS analysis of A point in Fig. 2.　　　TABLE II

Elem.	Line	Intensity [counts/s]	Error, 2-sig.	Concentration [wt.%]
C	Ka	112	6.692	45.107
O	Ka	4.75	1.378	8.160
Si	Ka	564	15.021	46.733

As is shown in Fig. 3, the SEM micrograph consists of fibrous particles of 50–100 nm in diameter. Very net shaped super nano-rods can easily be seen in Fig. 3. The SEM micrograph of Fig. 3 shows ultra-high aspect ratio of the particles. It is apparent that in Fig. 3 the SiC super nanorods are generally straight and have a preferential axis orientation and in addition interact with each other. Y.H. Gao et al. [16] and F. Çalışkan et al. [17] revealed that the axis of orientation of the SiC is constant along the length of the nanorod.

EDS analysis of B point in Fig. 2.   TABLE III

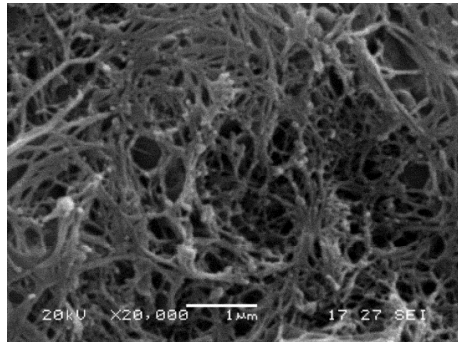| Elem.	Line	Intensity [counts/s]	Error, 2-sig.	Concentration [wt.%]
C	Ka	0.00	0.000	0.000
O	Ka	76.85	5.544	47.702
Si	Ka	43.91	3.093	13.791

Fig. 3. SiC particles after CRC at 1550 °C for 4 h, synthesized from the sample added with 5 wt.% of SiC and 5 wt.% of B₄C nucleants.

During the in-situ synthesis of the SiC-B$_4$C composites, after heating the powder mixture with the stoichiometric ratio to the reaction of components, the glassy phase was observed, shown in Fig. 4. It is clear that the SiC particles were covered by boron oxide glass. This can be due to reaction from Eq. (5), because B$_4$C can react with SiO$_2$ and can form B$_2$O$_3$ plus carbon and SiC. Authors think that while this mechanism supports SiC formation, the decomposition of B$_4$C to B$_2$O$_3$ increases with the increase of B$_4$C. EDS analysis in Fig. 4b shows that B and O elements were detected together instead of B and C. This observation supports B$_4$C decomposition mechanism and formation of the glassy phase.
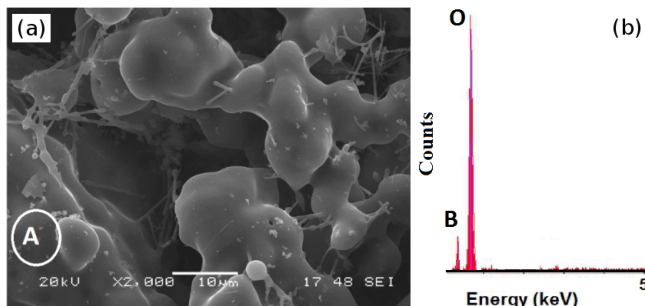

Fig. 4. (a) SEM image of sample with composition nr 7 after CRC conversion at 1550 °C (a), EDS analysis of region A (b).

As seen in Fig. 2, the XRD results are in accordance with SEM and EDS analyses. Authors think that such process can result in perfectly bonded fiber-matrix interface after sintering, as can be seen in Fig. 4a.

4. Conclusions

Present paper is focused on the synthesis of SiC-B$_4$C composite powder by CRC method. In this study the targeted objectives were achieved by processing the samples at 1550 °C for 4 h. Ultra-fine SiC nanorods with a diameter of 50–100 nm and net shaped very fine fibrous particles have been synthesized by CRC reaction. While SiC was the constantly dominant phase, B$_4$C has been the reinforcing phase. B$_2$O$_3$ glassy phase formation owing to the reaction between SiO$_2$ and B$_4$C was observed at high B$_4$C/SiO$_2$ ratios. Authors think that after sintering the synthesized SiC-B$_4$C composite powder will exhibit superior hardness, higher fracture toughness, higher compressive strength etc. than those of SiC-B$_4$C powder mixture, prepared by conventional mixing methods. In conclusion, ultrafine SiC-B$_4$C composite ceramic powder could be synthesized by an inexpensive CRC process. In addition, SiC-B$_4$C particles were significantly homogeneously distributed via the CRC method and the mismatch between the matrix and the reinforcement was minimized.

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