

# EFFECT OF COMPOSITION ON THE CHARACTERISTICS OF C-SiC-B<sub>4</sub>C COMPOSITES

A. Mishra, M. Saha, G. Bhatia, R. K. Aggarwal, V. Raman and P.R. Sengupta  
*Carbon Technology Unit, Division of Engineering Materials*  
*National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi - 110 012*

*Corresponding author e-mail address: ghatia@mail.nplindia.ernet.in*

## **Abstract**

C-SiC-B<sub>4</sub>C composites refer to a special class of carbon based materials which cover the main drawbacks of carbon, particularly its proneness to air oxidation, while essentially retaining its good properties. In the present paper, the authors report the results of a systematic study made towards the development of C-SiC-B<sub>4</sub>C composites, which involves the effects of carbon-to-ceramic and ceramic-to-ceramic ratios on the oxidation behaviour as well as other characteristics of these composites. The C-SiC-B<sub>4</sub>C composites, heat-treated to 1400 °C, have shown that their oxidation behaviour at temperatures of 800–1200 °C depends strongly on the total ceramic content and the SiC : B<sub>4</sub>C ratio. A total ceramic content of at least 52.3% (by weight of carbon) appears to be necessary, coupled with a SiC : B<sub>4</sub>C ratio of 60 : 40, to obtain C-SiC- B<sub>4</sub>C composites exhibiting high oxidation resistance at 800 and 1200 °C. Significant improvement in the strength of C-SiC-B<sub>4</sub>C composites has been observed which increases with an increase in the total ceramic content and the SiC : B<sub>4</sub>C ratio.

## **1. Introduction**

Carbon is a very fascinating material finding ever increasing applications in both industrial as well as strategic fields. This is because of its unique characteristics such as light weight, high temperature withstandability (without loss of strength) upto ~ 2500 °C in non-oxidising atmospheres, low coefficient of thermal expansion and friction, good electrical and thermal conductivities, and high thermal shock resistance [1–3]. However, it has few short-comings [4] also, e.g., high susceptibility to attack by the atmospheric oxygen which starts at a temperature of around 400 °C [3], low mechanical strength and high porosity. Here, this proneness of carbon to oxidation is a serious drawback, as it acts as a limitation to the use of carbon materials upto temperatures lower than ~400 °C. To overcome this shortcoming, two broad ways have been adopted [3–13] – one involving coating of the surface of carbon by materials like noble metals, borates, borosilicates, phosphates, carbides, nitrides etc., using techniques of chemical vapour deposition (CVD), impregnation or dipping etc., and the other involving addition of ceramic components such as B<sub>4</sub>C, SiC or TiC into the body of the carbon materials during their processing. The ultimate aim in both the cases is the formation of an impermeable protective layer over the surface of carbon. However, the latter method appears to be better of the two, as it not only protects the carbon from air oxidation but also leads to an improvement in its mechanical strength and a reduction in its open

porosity. Besides this, the resultant material, i.e., carbon-ceramic composites, are found to possess a unique self-healing property [7,8], which protects the material from oxidation in the event of any accidental or other damage.

Among the different carbon-ceramic composite systems, the C-SiC-B<sub>4</sub>C composites have been reported [8–13] to be an excellent system possessing high oxidation resistance at elevated temperatures. Though a number of papers are available in the literature on the oxidation resistance of this C-SiC-B<sub>4</sub>C system, no systematic attempt seems to have been reported so far which gives the effect of SiC : B<sub>4</sub>C ratio along with the effect of total ceramic (SiC+B<sub>4</sub>C) content on the oxidation behaviour as well as other characteristics of the C-SiC-B<sub>4</sub>C composites. In view of this, a study was conducted by the present authors in this direction, the results of which are reported in the present paper.

## **2. Experimental**

### ***2.1 Preparation of C-SiC-B<sub>4</sub>C composites***

A suitable coal tar pitch based self-sintering green coke powder, with an average particle size of about 6.5 μm, was first of all produced to act as the base carbonaceous material, using the process developed by Bhatia et al. [14]. Suitable quantities of commercial SiC and B<sub>4</sub>C powders with mean particle size of 5μm and 1μm, respectively, were then mixed with the green coke powder to obtain 15 different mixtures (batches), having compositions shown in Table -1. The mixtures were ground for 30 min. each to achieve a uniform dispersion of the three components in the mixtures. The mixtures were then compacted under a pressure of 2000 kg cm<sup>-2</sup>, using a hydraulic press to get the green plates of carbon-ceramic composites of dimensions 60mm x 20mm x 4 mm. The green composite plates were subjected to bulk density measurement and then carbonized to 1000 °C, which were further heat-treated to 1400 °C in an argon atmosphere.

### ***2.2 Investigation of various physical and mechanical properties***

All the heat-treated plates (HTT = 1000 /1400 °C) were characterised with respect to weight loss (WL), volume shrinkage (VS), linear shrinkage (LS), bulk density (BD), electrical resistivity (ER) and bending strength (BS) and the values obtained are summarised in Table -2.

### ***2.3 Investigation of isothermal oxidation behaviour***

The composite plates, heat-treated to 1400 °C, were cut into small specimens of 18 mm x 9 mm x 2 mm size, the surfaces of which were polished carefully with fine-grained emery papers. To carry out the oxidation tests, the specimens were first heated to the desired temperatures in an argon atmosphere, which was suddenly changed to air atmosphere under which the oxidation was carried out for different periods of time, after which the atmosphere was again changed to argon under which the samples were

cooled down to the room temperature. Tables -3(a-c) give summaries of the weight loss behaviour of the C-SiC-B<sub>4</sub>C composites of different batches of the three series (A-C) at temperatures of 800–1200 °C.

TABLE-1

COMPOSITIONS OF VARIOUS SERIES AND BATCHES OF C-SiC-B<sub>4</sub>C COMPOSITES

Series	SiC+B <sub>4</sub> C content (by wt. of carbon)	Batches	SiC : B <sub>4</sub> C ratio (wt %)
A	33.3	1	60.0 : 40.0
		2	66.7 : 33.3
		3	75.0 : 25.0
		4	80.0 : 20.0
		5	87.5 : 12.5
B	42.9	1	60.0 : 40.0
		2	66.7 : 33.3
		3	75.0 : 25.0
		4	80.0 : 20.0
		5	87.5 : 12.5
C	53.8	1	60.0 : 40.0
		2	66.7 : 33.3
		3	75.0 : 25.0
		4	80.0 : 20.0
		5	87.5 : 12.5

### 3. Results and Discussion

#### 3.1 Physical and Mechanical behaviour

Table-2 gives a summary of the various physical and mechanical properties of the C-SiC-B<sub>4</sub>C composite plates of various series and batches having compositions as shown in Table-1. It is seen from Tables-1&2 that the green density of the C-SiC-B<sub>4</sub>C composite plates increases as the overall ceramic content in the plates increases. Further, even in a particular Series-A, B or C, the density of the plates increases with an increase in the proportion of SiC content. These observations are clearly explainable from the knowledge of bulk densities of green coke, SiC and B<sub>4</sub>C powders. The weight loss of the plates, on carbonisation to 1000 °C, is also seen to decrease, as one moves from Series-A (5.9–6.9%) to Series-C (4.6–5.1%) through the Series-B (6.5–6.8%). This is quite understandable, as it is only the green coke component of the plates, which undergoes weight loss in the form of volatiles. However, upon further heat-treatment of the plates to 1400 °C, the weight loss, surprisingly, remains the same (varying in the range of 7.1–7.8%) in all the three series (A–C). However, for any batch, as expected, the weight loss at a HTT of 1400 °C is higher than what it is at a HTT of 1000 °C.

TABLE-2

CHARACTERISTICS OF C-SiC-B<sub>4</sub>C COMPOSITES (HTT = 1400 °C) HAVING DIFFERENT COMPOSITIONS

Series Batch	Characteristics of C-SiC-B <sub>4</sub> C composites						
	GD	WL	VS	LS	BD	BS	ER
A-1	1.48	7.8 (6.9)	25.8 (23.9)	9.0 (7.8)	1.83 (1.78)	42	4.5
A-2	1.49	7.7 (6.8)	25.6 (23.6)	9.0 (7.8)	1.84 (1.79)	45	4.5
A-3	1.50	7.4 (6.5)	25.3 (23.5)	8.4 (7.6)	1.85 (1.84)	60	4.7
A-4	1.50	7.2 (6.0)	25.0 (23.1)	8.4 (7.5)	1.87 (1.85)	67	4.2
A-5	1.50	7.1 (5.9)	24.9 (23.0)	8.3 (7.5)	1.88 (1.86)	70	4.3
B-1	1.49	7.7 (6.8)	25.7 (25.5)	8.0 (7.3)	1.83 (1.82)	66	6.3
B-2	1.50	7.6 (6.7)	25.2 (25.1)	8.0 (7.3)	1.84 (1.83)	66	5.8
B-3	1.52	7.5 (6.7)	25.0 (23.3)	8.0 (7.3)	1.85 (1.84)	67	4.9
B-4	1.53	7.5 (6.6)	24.9 (22.3)	7.9 (7.3)	1.85 (1.84)	67	6.3
B-5	1.54	7.2 (6.5)	24.7 (21.2)	7.9 (7.2)	1.87 (1.85)	72	5.2
C-1	1.55	7.8 (5.1)	22.2 (21.0)	7.8 (6.4)	1.88 (1.84)	77	5.0
C-2	1.55	7.3 (4.8)	22.0 (20.6)	7.8 (6.4)	1.89 (1.84)	78	4.9
C-3	1.55	7.3 (4.8)	22.0 (20.4)	7.6 (6.4)	1.90 (1.85)	82	4.5
C-4	1.58	7.2 (4.6)	21.9 (18.0)	7.4 (6.3)	1.91 (1.86)	83	5.0
C-5	1.60	7.2 (4.6)	21.6 (17.5)	7.4 (6.3)	1.92 (1.88)	90	5.1

- NOTE : 1. GD = Green Density (g cm<sup>-3</sup>); WL = Weight Loss (%); VS = Volume Shrinkage (%); LS = Linear Shrinkage (%); BD = Bulk Density (g cm<sup>-3</sup>); BS= Bending Strength (MPa); ER = Electrical Resistivity (m ohm cm).
2. The values in parentheses refer to HTT = 1000 °C.

The volume shrinkage of the plates, at both the HTTs (1000 / 1400 °C), is found to decrease as one moves from Series-A to Series-C, exhibiting values of 23.0–23.9% for Series-A, 21.2–25.5% for Series-B and 17.5–21.0% for Series-C at a HTT of 1000 °C, and values of 24.9–25.8% for Series-A, 24.7–25.5% for Series-B and 21.6–22.2% for Series-C at a HTT of 1400 °C. Further, for any batch, the volume shrinkage at a HTT of 1400 °C is seen to be higher than its value at a HTT of 1000 °C. As the volume shrinkage is associated with the weight loss, the variations in the volume shrinkage of the different series or batches are found to be quite consistent with the variations of their weight loss, at any HTT–1400 or 1000 °C. The linear shrinkage, being directly linked with the volume shrinkage, is seen to follow essentially the same trend as the volume shrinkage.

As the bulk density of the plates, upon any heat-treatment, involves the effects of weight loss and volume shrinkage in the bulk density of the plates in the green stage (green density), it is found to be in complete agreement with the variations in the green density, weight loss and volume shrinkage of the plates, occurring at any HTT– 1400 or 1000 °C. The overall effect is a nominal increase in its value as one moves from Series-A to Series-C, at both the HTTs, and also a marginally higher value at a HTT of 1400 °C compared to a HTT of 1000 °C.

The bending strength of the plates, heat-treated to 1400 °C, is seen to increase with the increase in the total ceramic content in the composition as well as with the increase in the SiC proportion in the total ceramic content. Accordingly, it increases from values of 42–70 MPa for Series-A to 66–72 MPa for Series-B and finally 77–90 MPa for Series-C. These observations may be explained as the result of hindrance to the proportion of cracks by the presence of strong ceramic particles in the body of the C-SiC-B<sub>4</sub>C composite plates, besides due to a reduction in their porosity. The electrical resistivity of the plates does not seem to follow any fixed trend with the total ceramic content or the ceramic-to-ceramic ratio.

### **3.2 Oxidation behaviour**

Tables-3 (a–c) give a summary of the weight loss of C-SiC-B<sub>4</sub>C composite plates, heat-treated to 1400 °C, having different ceramic content and SiC : B<sub>4</sub>C ratio, when these plates are subjected to air oxidation at temperatures of 800–1200 °C for periods of 1–10 h. It is observed that, in general, for a particular batch and for a particular temperature, the cumulative weight loss goes on increasing with the residence time upto a stage after which there is no or nominal weight loss with further increase in the residence time. This stage refers to the formation of a protective layer over the surface of the carbon, the composition of which will depend upon the total ceramic content and the temperature of oxidation. Further, depending upon the composition of the protective layer and the coverage of the carbon surface by the protective layer, will depend the effectiveness of the layer to protect the carbon from air oxidation.

It is well known that during the air oxidation of C-SiC-B<sub>4</sub>C composites, B<sub>4</sub>C starts getting converted into glassy B<sub>2</sub>O<sub>3</sub> layer at a temperature ~ 500 °C, while the SiC conversion into SiO<sub>2</sub> starts at a temperature of ~ 800 °C, at which the evaporation of B<sub>2</sub>O<sub>3</sub> also starts. Upto a temperature of ~ 800 °C, the protection of carbon is provided by the formation of B<sub>2</sub>O<sub>3</sub> layer, while above 800 °C, it is the eutectic solution of B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, which actually protects the carbon surface from air oxidation. According to Ogawa et al. [4] and Quangui Guo et al. [8], a B<sub>2</sub>O<sub>3</sub>-rich composition of the B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> eutectic solution provides oxidation resistance at temperatures of 800–1000 °C, while a SiO<sub>2</sub>-rich composition is preferable for oxidation resistance at temperatures above 1000 °C.

It may be further observed from the results summarised in Tables-2&3 (a–c), that in general, for a particular SiC : B<sub>4</sub>C ratio and a particular temperature of oxidation, the value of weight loss, particularly for the maximum period (10 h) of air oxidation, goes on decreasing as the total ceramic content in the composite plates increases from 33.3 to 53.8%. This is clearly the result of increasingly higher effectiveness of the protective layer formed over the surface of carbon because of the availability of increasingly higher amount of total ceramic content in carbon-ceramic composites.

It is interesting to note that at 800 °C, the C-1 and C-2 batches show negative values of weight loss, thereby referring to weight gain upon air oxidation. In fact, this weight in gain is the overall result of two types of oxidative reactions, which take place

TABLE-3 (a)  
 WEIGHT LOSS BEHAVIOUR OF C-SiC-B<sub>4</sub>C COMPOSITE PLATES (HTT = 1400 °C)  
 OF DIFFERENT BATCHES OF SERIES-A UPON AIR OXIDATION AT (800-1200) °C

Series-Batch	Temperature (°C)	Cumulative weight loss upon air oxidation for different periods of time					
		1h	2h	4h	6h	8h	10h
A-1	800	5.6	6.1	8.5	8.6	8.6	8.6
	1000	5.7	7.3	8.7	9.9	9.9	9.9
	1200	10.0	12.3	13.3	13.3	–	–
A-2	800	5.3	6.0	14.1	14.4	14.4	14.4
	1000	6.5	10.3	12.3	13.3	13.8	14.0
	1200	31.2	33.7	35.6	37.1	–	–
A-3	800	4.3	7.2	19.4	19.4	19.5	19.7
	1000	8.2	19.8	24.9	27.2	27.6	28.0
	1200	23.7	26.4	28.5	29.9	–	–
A-4	800	3.2	8.2	29.2	31.4	32.3	32.9
	1000	12.1	29.7	46.3	55.6	59.1	61.4
	1200	17.9	23.6	27.1	28.7	–	–
A-5	800	23.3	32.7	68.6	70.4	71.3	72.1
	1000	50.6	66.2	75.9	78.8	80.6	81.5
	1200	14.7	31.8	39.0	45.8	–	–

TABLE-3 (b)  
 WEIGHT LOSS BEHAVIOUR OF C-SiC-B<sub>4</sub>C COMPOSITE PLATES (HTT = 1400 °C)  
 OF DIFFERENT BATCHES OF SERIES-B UPON AIR OXIDATION AT (800-1200) °C

Series-Batch	Temperature (°C)	Cumulative weight loss upon air oxidation for different periods of time					
		1h	2h	4h	6h	8h	10h
B-1	800	3.3	4.3	8.1	8.3	8.3	8.3
	1000	4.4	6.8	8.3	9.1	9.1	9.1
	1200	3.0	3.2	6.2	8.5	–	–
B-2	800	2.7	4.8	9.0	9.1	9.4	9.5
	1000	7.2	8.5	9.2	9.8	9.8	9.8
	1200	10.1	12.4	13.5	13.5	–	–
B-3	800	4.8	5.8	9.8	9.8	10.2	10.6
	1000	7.2	14.3	19.3	21.8	22.1	22.8
	1200	8.9	11.7	13.0	13.2	–	–
B-4	800	5.4	7.5	11.1	11.4	12.0	12.4
	1000	9.0	19.4	29.2	41.3	44.5	45.2
	1200	8.9	12.4	14.9	15.0	–	–
B-5	800	14.8	23.3	57.3	58.4	58.9	59.2
	1000	41.3	50.1	55.8	66.7	70.0	71.4
	1200	10.0	21.3	21.3	22.3	–	–

TABLE-3 (c)

WEIGHT LOSS BEHAVIOUR OF C-SiC-B<sub>4</sub>C COMPOSITE PLATES (HTT = 1400 °C) OF DIFFERENT BATCHES OF SERIES-C UPON AIR OXIDATION AT (800–1200) °C

Series-Batch	Temperature (°C)	Cumulative weight loss upon air oxidation for different periods of time					
		1h	2h	4h	6h	8h	10h
C-1	800	-1.6	-2.4	-2.0	-2.0	-2.0	-2.0
	1000	4.5	5.7	6.4	6.7	6.8	6.8
	1200	2.3	2.3	2.3	2.3	2.3	2.3
C-2	800	-0.9	-0.3	-0.3	-0.2	-0.2	-0.2
	1000	8.3	9.2	9.7	9.9	9.9	9.9
	1200	4.3	5.6	5.8	5.8	–	–
C-3	800	4.4	4.6	6.0	6.5	6.6	6.6
	1000	9.8	19.8	24.9	27.2	27.6	27.8
	1200	4.5	12.4	14.9	15.3	–	–
C-4	800	4.4	4.6	6.0	6.5	6.6	6.6
	1000	8.2	19.8	24.9	27.2	27.6	27.9
	1200	4.5	11.7	13.0	13.2	–	–
C-5	800	10.7	21.7	26.0	50.7	51.1	52.7
	1000	12.3	37.5	54.5	57.2	57.8	58.0
	1200	6.5	15.1	17.2	17.4	–	–

simultaneously when C-SiC-B<sub>4</sub>C composites are exposed to air oxidation – one is the oxidation of carbon to CO<sub>2</sub> / CO which results in a loss of weight of the composites, and the other is the oxidation of SiC into SiO<sub>2</sub> and B<sub>4</sub>C into B<sub>2</sub>O<sub>3</sub>, both of which lead to a gain in weight of the composites.

A close examination of the results shown in Tables-2&3 (a–c) reveals that the C-1 batch is able to provide high oxidation resistance (maximum weight loss = 2–3 %) at temperatures of 800 and 1200 °C, while leading also to sufficiently high mechanical strength of the C-SiC-B<sub>4</sub>C composites. However, at 1000 °C, though the same C-1 batch exhibits the minimum value of weight loss of 6.8 % out of all the batches, it can not be regarded as satisfactory. In view of this, further studies towards increasing the overall ceramic content in the composition or decreasing the SiC : B<sub>4</sub>C ratio appear to be necessary.

#### 4. Conclusions

1. Studies conducted on the C-SiC-B<sub>4</sub>C composites, heat-treated to 1400 °C, reveal that their oxidation behaviour at temperatures of 800–1200 °C depends strongly on the total ceramic (SiC + B<sub>4</sub>C) content and the SiC : B<sub>4</sub>C ratio.

2. A total ceramic content of at least 52.3% (by weight of carbon) appears to be necessary, coupled with a SiC : B<sub>4</sub>C ratio of 60 : 40, to obtain C-SiC- B<sub>4</sub>C exhibiting high oxidation resistance (maximum weight loss = 2–3%) at 800 and 1200 °C. However, no satisfactory composition could be identified, which shows high oxidation resistance at 1000 °C.

3. Significant improvement in the strength of C-SiC- B<sub>4</sub>C composites takes place because of the presence of SiC and B<sub>4</sub>C particles. This improvement is observed to increase with an increase in the total ceramic content and the SiC : B<sub>4</sub>C ratio.

4. The electrical resistivity of the C-SiC- B<sub>4</sub>C composites does not seem to follow any fixed trend with the total ceramic content or the ceramic-to-ceramic ratio.

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