

Effect of Compositional Parameters on the Characteristics of C-SiC-B₄C Composites

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Abstract

Carbon-ceramic 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 outstanding properties. In the present paper, the authors report the results of a systematic study made towards the development of C-SiC-B₄C composites, which involves the effects of compositional parameters, namely, carbon-to-ceramic and ceramic-to-ceramic ratios, on the oxidation behaviour as well as other characteristics of these composites. The C-SiC-B₄C composites, heat-treated to 1400 °C, have shown that their oxidation behaviour at temperatures of 800~1200 °C depends jointly on the total ceramic content and the SiC : B₄C ratio. Good compositions of C-SiC-B₄C composites exhibiting zero weight loss in air at temperatures of 800~1200 °C for periods of 4~9 h, have been identified. Composites with these compositions undergo a weight gain or a maximum weight loss of less than 3% during the establishment of a protective layer at the surface of carbon in a period of 1~6 h. Significant improvement in the strength of C-SiC-B₄C composites has been observed which increases with an increase in the total ceramic content and also with an increase in the SiC : B₄C ratio.

Keywords : Carbon-ceramic composites, C-SiC-B₄C composites, Oxidation resistance

1. Introduction

Carbon and graphite materials are widely used in a large number of applications because of their unique characteristics such as light weight, high temperature withstandability (without loss of strength) in non-oxidising atmospheres, low coefficient of thermal expansion and friction, good electrical and thermal conductivities, and high thermal shock resistance [1-3]. However, these materials have 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 in air upto temperatures of around 400 °C. To overcome this short-coming, 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 B₄C, 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 air oxidation in the event of any accidental or other damage.

Among the different carbon-ceramic composite systems, the C-SiC-B₄C 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-B₄C system, no systematic work seems to have been reported so far which gives the effect of SiC : B₄C ratio along with the effect of total ceramic (SiC+B₄C) content on the oxidation behaviour as well as other characteristics of the C-SiC-B₄C composites. In view of this, a detailed study was carried out by the authors in this direction, the results of which are reported in the present paper.

2. Experimental

2.1. Preparation of C-SiC-B₄C 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,

Table 1. Compositions of various series and batches of C-SiC-B₄C composites

Series	SiC+B ₄ C content (% by wt. of carbon)	Batches	SiC : B ₄ 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
D	66.7	1	50.0 : 50.0
		2	66.7 : 33.3
		3	75.0 : 25.0

using the process developed by Bhatia *et al.* [14]. Suitable quantities of commercial SiC and B₄C powders with mean particle size of 5 μm and 1 μm, respectively, were then mixed with the green coke powder to obtain 18 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⁻² using a hydraulic press to get green plates of the carbon-ceramic composites of dimensions 60 mm × 20 mm × 4 mm. These plates were subjected to bulk density measurement and then carbonised to 1000 °C. The resultant plates 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 × 9 mm × 2 mm size, the surfaces of which were polished carefully using 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 an air atmosphere under which the oxidation was carried out for different periods of time, after which the air atmosphere was again changed to an argon atmosphere under which the samples were cooled down to the room temperature. Tables 3(a~d)

Table 2. Characteristics of C-SiC-B₄C composites (HTT = 1400 °C) having different compositions

Series-Batch	Characteristics of C-SiC-B ₄ 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)	7.3 (8.0)	1.83 (1.82)	66	6.3
B-2	1.50	7.6 (6.7)	25.2 (25.1)	7.3 (8.0)	1.84 (1.83)	66	5.8
B-3	1.52	7.5 (6.7)	25.0 (23.3)	7.3 (8.0)	1.85 (1.84)	67	4.9
B-4	1.53	7.5 (6.6)	24.9 (22.3)	7.3 (7.9)	1.85 (1.84)	67	6.3
B-5	1.54	7.2 (6.5)	24.7 (21.2)	7.2 (7.9)	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
D-1	1.61	5.5 (4.9)	21.0 (17.9)	7.8 (7.1)	1.91 (1.83)	102	4.7
D-2	1.62	5.4 (4.7)	20.5 (17.2)	7.7 (6.9)	1.92 (1.86)	110	4.8
D-3	1.63	5.3 (4.5)	19.9 (16.4)	7.5 (6.7)	1.95 (1.89)	119	4.4

NOTE: 1. GD = Green Density (g cm⁻³); WL = Weight Loss (%); VS = Volume Shrinkage (%); LS = Linear Shrinkage (%); BD = Bulk Density (g cm⁻³); BS = Bending Strength (MPa); ER = Electrical Resistivity (m ohm cm)

2. Values in parentheses refer to a HTT = 1000 °C

Table 3. (a) Weight loss behaviour of C-SiC-B₄C 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-B₄C 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	–	–

give summaries of the weight loss behaviour of the C-SiC-B₄C composites of different batches of the four series (A~D) at temperatures of 800~1200 °C. The surface morphology of some of the specimens was also studied using a Scanning Electron Microscope (SEM), and the micrographs obtained are shown in Figs. 1~4.

Table 3. (c) Weight loss behaviour of C-SiC-B₄C 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	–	–

Table 3. (d) Weight loss behaviour of C-SiC-B₄C composite plates (HTT = 1400 °C) of different batches of Series-D 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
D-1	800	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4
	1000	0.6	0.7	0.7	0.7	0.7	0.7
	1200	-0.6	-7.6	-5.1	2.8	2.8	2.8
D-2	800	0.4	0.4	0.4	-0.2	-0.3	-0.3
	1000	0.9	0.9	1.3	1.3	1.3	1.3
	1200	0.2	0.3	0.5	2.4	2.6	2.6
D-3	800	1.2	1.3	1.3	1.4	1.9	2.1
	1000	1.0	1.0	1.5	1.5	1.5	1.5
	1200	0.5	0.9	1.7	2.1	2.3	2.3

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-B₄C 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-B₄C composite plates increases as the overall ceramic content in the plates increases. Further, even in a particular series-A, B, C or D, the density of the plates increases with an increase in the proportion of the SiC content. These observations are clearly explainable from the

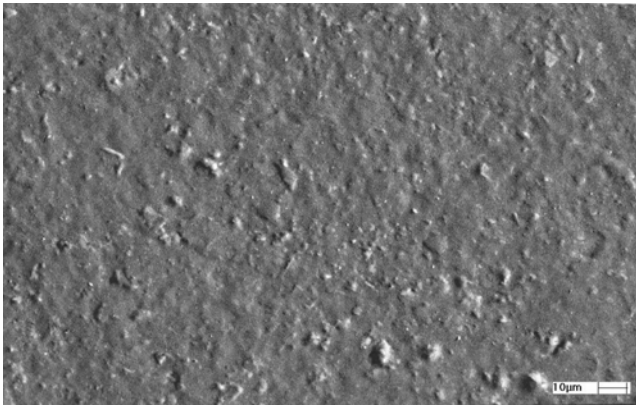


Fig. 1. SEM photograph of C-SiC-B₄C composites of D-1 batch, without any air oxidation.



Fig. 2. SEM photograph of C-SiC-B₄C composites of D-1 batch, upon oxidation in air at 800 °C for 1h.

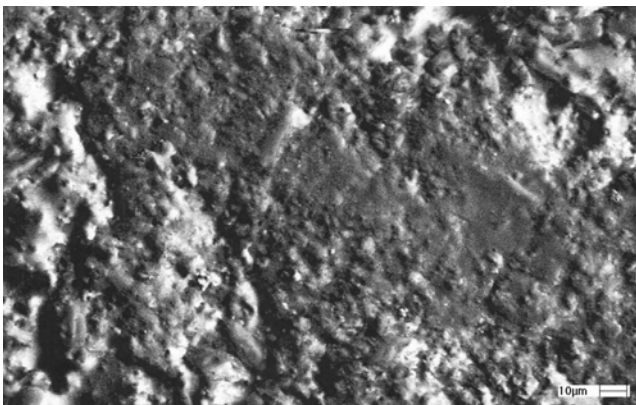


Fig. 3. SEM photograph of C-SiC-B₄C composites of D-1 batch, upon oxidation in air at 1000 °C for 2h.

knowledge of bulk densities of the green coke, and the SiC and B₄C powders. The weight loss of the plates, on carbonisation to 1000 °C, is seen to decrease, as one moves from Series-A (5.9~6.9%) to Series-B (6.5~6.8%), Series-C

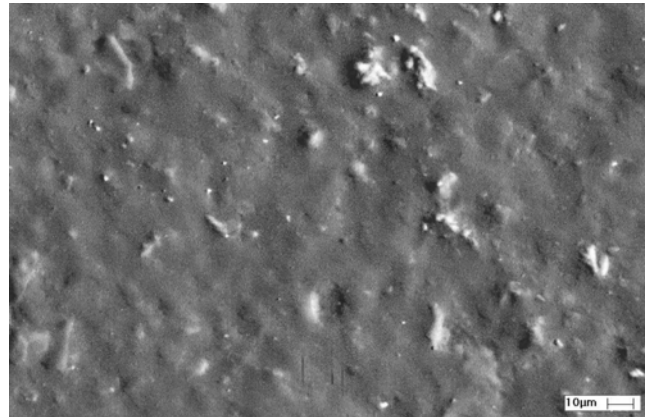


Fig. 4. SEM photograph of C-SiC-B₄C composites of D-1 batch, upon oxidation in air at 1200 °C for 6h.

(4.6~5.1%) and finally Series-D (4.5~4.9%). This is quite understandable, as it is only the green coke component of the plates, which is undergoing 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 the case of first three series (A~C), but decreases significantly to a value of (5.3~5.5%) in the case of Series-D. This sudden decrease in the weight loss in the case of Series-D may be due to the 'surface-induced carbonisation effect', taking place in a pronounced manner in the green coke component because of the presence of fine ceramic particles, to the highest extent of 66.7% by weight of carbon. Further, 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.

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-D, exhibiting values of 23.0~23.9% for Series-A, 21.2~25.5% for Series-B, 17.5~21.0% for Series-C and 16.4~17.9% for Series-D at a HTT of 1000 °C, and values of 24.9~25.8% for Series-A, 24.7~25.7% for Series-B, 21.6~22.2% for Series-C and 19.9~21.0% for Series-D 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 °C 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 on 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 °C or

1000 °C. The overall effect is a nominal increase in its value as one moves from Series-A to Series-D, at both the HTTs, and 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 an increase in the total ceramic content in the composition as well as with an 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, 77~90 MPa for Series-C and finally 102~119 MPa for Series-D. These improvements in the bending strength may be explained as the result of hindrance to the propagation of cracks by the presence of strong ceramic particles in the body of the C-SiC-B₄C composite plates, besides due to a probable reduction in their open porosity. It may be emphasised here that the values of 102~119 MPa obtained in the case of Series-D refer to considerably higher values of the bending strength compared to that of the green coke based carbons heat-treated to 1400 °C. The electrical resistivity of the plates, in turn, varies in the range of 4.2~6.3 mΩ cm, following no fixed trend with the total ceramic content or the ceramic-to-ceramic ratio.

3.2. Oxidation behaviour

Tables 3(ad) give summaries of the cumulative weight loss of C-SiC-B₄C composite plates, heat-treated to 1400 °C, of the four series (A~D) having different total ceramic content and the SiC : B₄C ratio, when the plates of these series 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, there is a weight loss initially, which goes on increasing with an increase in the time of residence 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 or establishment of a protective layer at the surface of the carbon, the effectiveness of which will depend broadly upon the total ceramic content and the SiC and B₄C components in it, as well as on the temperature of oxidation. In certain cases, instead of weight loss, there is found to be a weight gain initially, which is followed by further weight gain or weight loss or constancy of weight upto a stage after which the composites show zero weight loss with further increase in the time of residence.

In fact, this weight loss or weight gain is the overall result of two types of oxidative reactions, which take place simultaneously at different rates when C-SiC-B₄C composites are exposed to air oxidation – one is the oxidation of carbon to CO₂/CO which results in a loss in weight of the composites, and the other is the oxidation of SiC into SiO₂ and B₄C into B₂O₃, both of which lead to a gain in weight of the composites.

It is well known that during the exposure of C-SiC-B₄C composites to air, B₄C starts getting converted into glassy

B₂O₃ layer at a temperature of ~500 °C, while the SiC conversion into SiO₂ starts at a temperature of ~800 °C, at which rapid evaporation of B₂O₃ takes place. Upto a temperature of ~800 °C, the protection of carbon is provided by the formation of B₂O₃ layer, while above 800 °C, it is the eutectic solution of B₂O₃-SiO₂ which protects the carbon from air oxidation. According to Ogawa *et al.* [4] and Quangui Guo *et al.* [8], a B₂O₃-rich composition of the B₂O₃-SiO₂ eutectic solution provides oxidation resistance at temperatures of 800~1000 °C, while a SiO₂-rich composition is preferable for oxidation resistance at temperatures above 1000 °C.

It may be further observed from the results summarised in Tables 3(a~d) that, in general, for a particular SiC : B₄C 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 66.7%. This is clearly the result of increasingly higher effectiveness of the protective layer formed at the surface of carbon because of the availability of increasingly higher amount of the total ceramic content in the carbon-ceramic composites.

Further, it is seen that in all the batches of Series-A or B, the maximum weight loss is much more than 3%, the highest value (of weight loss) set by the present authors to be acceptable. Furthermore, in Series-C, the C-1 batch is observed to show a weight gain of 2.0% at 800 °C and a maximum weight loss of 2.3% at 1200 °C. Besides this, the C-2 batch also shows a weight gain at 800 °C. In other words, an overall ceramic content of 53.8%, jointly with a SiC : B₄C ratio of 60 : 40/66.7 : 33.3, or 60:40 can provide good oxidation resistance at temperatures of 800 °C or 1200 °C, respectively. However, it may be observed that it is only in the case of Series-D (having an overall ceramic content of 66.7%) that in all batches, the maximum weight loss at all the temperatures of oxidation in the range of 800~1200 °C is less than 3%. At 800 °C, there is even a gain in weight. This clearly indicates the importance of overall ceramic content in the C-SiC-B₄C composites. Even in this series, the D-1 batch appears to be the best, exhibiting the lowest or near lowest (for 1200 °C) values of the weight loss at all the temperatures in the range of 800~1200 °C. Besides this, the time taken to arrive at the saturation values is also the lowest.

Figs. 1~4 show the SEM photographs of the samples of D-1 batch exposed to temperatures of 800~1200 °C in air for periods of 1~6 h, vis-à-vis the unoxidised sample. It can be seen that in all the cases of air oxidation, there is an excellent formation of smooth glassy protective layer of borosilicate over the whole surface of carbon. In none of the cases, any uncovered patches of carbon surface (or holes in the protective layer) is seen. This is in complete agreement with the oxidation behaviour of the C-SiC-B₄C composites in these cases showing zero weight loss during further heat-treatment in air for periods upto 10 h.

4. Conclusions

1. The oxidation resistance of C-SiC-B₄C composites, heat-treated to 1400 °C, at temperatures of 800~1200 °C depends jointly on the total ceramic (SiC+B₄C) content as well as the SiC : B₄C ratio.

2. A total ceramic content of 66.7% (by weight of carbon), coupled with a SiC : B₄C ratio of 50 : 50 (by weight), appears to provide a good composition of C-SiC-B₄C composites exhibiting high oxidation resistance at all temperatures in the range of 800~1200 °C. Besides this, a lower value of 53.8% of the overall ceramic content, accompanied with SiC : B₄C ratios of 60 : 40/66.7 : 33.3, or 60 : 40 is also found to be good for application temperatures of 800 °C or 1200 °C, respectively.

3. Significant improvement in the strength of C-SiC-B₄C composites has been observed which increases with an increase in the total ceramic content and also with an increase in the SiC : B₄C ratio.

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References

- [1] Marsh, H.; Heintz, E. A.; Rodriguez-Reinoso, F. *Introduction to Carbon Technologies*; ed. H. Marsh, University of Alicante, Spain, 1997.
- [2] Ishikawa, T.; Nagaoki, T. *Recent Carbon Technologies*; ed. I. C. Lewis (English editor), JEC Press, Japan, 1983.
- [3] McKee, D. W. *Chemistry and Physics of Carbon*; Vol. 23, ed. P.A. Thrower, Marcel Dekker, New York, 1991, 173.
- [4] Ogawa, I.; Kobayashi, K.; Nishikawa, S. *J. Mater. Sci.* **1988**, *23*, 1363.
- [5] McKee, D. W. *Carbon*. **1987**, *25*, 551.
- [6] McKee, D. W. *Carbon*. **1988**, *26*, 659.
- [7] Guo, Q.; Song, J.; Liu, L.; Zhang, B. *Carbon* **1998**, *36*, 1597.
- [8] Guo, Q.; Song, J.; Liu, L.; Zhang, B. *Carbon* **1999**, *37*, 33.
- [9] Kobayashi, K.; Miazaki, K.; Ogawa, I.; Haigo, T.; Yoshida, H. *Materials & Design*. **1988**, *9*, 10.
- [10] Kobayashi, K.; Maeda, K.; Sano, H.; Uchiyama, H. *Carbon* **1995**, *33*, 397.
- [11] Kobayashi, K.; Maeda, K.; Uchiyama, Y. *TANSO*. **1992**, *151*, 20.
- [12] Zhang, W. G.; Cheng, H. M.; Sano, H.; Uchiyama, Y.; Kobayashi, K.; Zhou, L. J.; Shen, Z. H.; Zhou, B. L. *Carbon* **1998**, *36*, 1591.
- [13] Fan, Z.; Song, Y.; Li, J.; Liu, L.; Song, J.; Chen, J.; Zhai, G.; Shi, J. *Carbon* **2003**, *41*, 429.
- [14] Bhatia, G.; Aggarwal, R. K.; Bahl, O. P. Proceedings of National Conference on Carbon, Kanpur, India, 1996, 182.