J Mater Sci (2009) 44:4633–4638
DOI 10.1007/s10853-009-3707-1

# Influence of coal tar pitch coating on the properties of micro and nano SiC incorporated carbon–ceramic composites

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Received: 2 March 2009 / Accepted: 23 June 2009 / Published online: 7 July 2009

**Abstract** Carbon-micro or nano silicon carbide–boron carbide (C-micro or nanoSiC–$B_4C$) composites were prepared by heating the mixtures of green coke and carbon black as carbon source, boron carbide and silicon at temperature of 1,400 °C. Green coke reacts with silicon to give micron sized silicon carbide while the reaction between silicon and carbon black gives nano silicon carbide in the resulting carbon–ceramic composites. The green coke was coated with a suitable coal tar pitch material and used to develop carbon-(micro or nano) silicon carbide–boron carbide composites in a separate lot. The composites were characterized for various properties including oxidation resistance. It was observed that both types of composites made from uncoated as well as pitch-coated green coke exhibited good oxidation resistance at 800–1,200 °C. The density and bending strength of composites developed with pitch-coated green coke improved significantly due to the enhanced binding of the constituents by the pitch.

## Introduction

Carbon products like high density, high strength, isotropic graphite, carbon–carbon composites find a large number of applications in general engineering as well as in many strategic areas like aerospace and defence due to their excellent thermal, physical, chemical and mechanical properties, namely light weight, inertness to many chemicals, high strength and high modulus at elevated temperatures in inert atmosphere [1]. But serious limitation is faced when they have to be employed at temperature above 450 °C in air due to their susceptibility to oxidation [2]. This limitation was overcome to some extent by the development of carbon–ceramic composites, which are generally prepared by incorporating oxidation resistant ceramic carbides into the carbon substrate [3–7]. The authors had developed carbon–ceramic composites by incorporating silicon carbide (SiC) particulates as such as well as through in situ formation using SiC forming precursors and boron carbide ($B_4C$) into the in-house developed coal tar pitch based green coke (GC) [5, 7]. The authors also recently prepared carbon-nano SiC–$B_4C$ composites using silicon (Si) and carbon black (CB) as silicon carbide forming precursor and found that the weight gain on oxidation of these composites at 800–1,200 °C was higher compared to that in carbon-micro SiC–$B_4C$ composites due to the nano size SiC, which had also undergone oxidation around 800 °C [8]. The present article deals with the study of physical properties as well as oxidation resistance of carbon–ceramic composites developed with GC as such and GC coated with suitable pitch material since composites incorporated with nano silicon carbide may require more binding material for obtaining stronger composites. The influence of the coal tar pitch coating on properties of carbon-(micro or nano) silicon carbide–boron carbide composites was investigated and reported in this article.

## Experimental

### Development of green coke, pitch-coated green coke and carbon monolith

Green coke was prepared in-house by the suitable heat treatment of coal tar pitch free from quinoline insolubles at 450 °C,

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which was ball milled into a fine powder and used as such [8]. It was then coated with 2% (by weight) of coal tar pitch having a softening point of 188 °C and $\beta$-resin content of 51% using toluene as a solvent and the mixture was calcined at 250 °C under reduced pressure in inert atmosphere to remove the solvent and to get pitch-coated GC. The GC powder with and without pitch coating were moulded into rectangular plates of the size 40 mm × 10 mm × 5 mm using a conventional hydraulic press at a pressure of 1,450 kg/cm$^2$. These green plates were carbonized at a heat treatment temperature (HTT) of 1,000 °C in nitrogen atmosphere employing a heating rate of 20 °C/h upto 250 °C, 10 °C/h upto 750 °C and 15 °C/h upto 1,000 °C. The carbonized plates were further heat treated upto 1,400 °C by employing the heating rate of 100 °C/h upto 1,000 °C and 30 °C/h upto 1,400 °C in nitrogen atmosphere to get carbon monolith.

### Development of C-micro SiC–B$_4$C and C-nano SiC–B$_4$C composites

The C-micro SiC–B$_4$C and C-nano SiC–B$_4$C composites (batches A and C) were prepared at a HTT of 1400 °C with GC as such by the method reported earlier [8]. The same procedure was repeated by substituting GC with pitch-coated GC to develop C-micro SiC–B$_4$C and C-nano SiC–B$_4$C composite (batches B and D).

## Characterization

Carbon monolith and carbon–ceramic composites derived using GC as such and pitch-coated GC were characterized at room temperature (RT) for their bulk density, weight loss and volume shrinkage after their heat treatment at 1,000 and 1,400 °C, respectively. The bending strength of the carbon monolith and carbon–ceramic composites developed using both types of GC (as such and pitch coated), silicon, boron carbide and CB was also measured at RT after the heat treatment at 1,400 °C by three point bending test using Instron Universal Testing Machine (model 4411). The electrical resistivity was determined at RT using a laboratory developed apparatus employing four probe technique. The rectangular specimen of carbon–ceramic composite was fitted between two thick copper plates connected to power supply. A suitable current (1 A) was allowed to pass across the specimen and potential drop was measured with the help of precision micro-voltmeter using two pin probes. The electrical resistivity (ER) was then obtained from the following equation:

$$\mathrm{ER} = VA/IL$$

where ER is electrical resistivity of the test specimen ($\Omega$ cm), $V$ the potential drop across the probe pins (V), $A$ the area of cross-section of test specimen (cm$^2$), $I$ the magnitude of D.C. current (A) and $L$ the distance between the probes (cm).

The C-micro SiC–B$_4$C (batch B) and C-nano SiC–B$_4$C (batch D) developed with pitch-coated GC at a HTT of 1,400 °C were characterized by X-ray diffraction technique employing D-8 Advanced Bruker Powder X-ray diffractometer using Cu$K_\alpha$ radiation ($\lambda = 1.5418$ Å) spectrometer. The composite samples of C-micro SiC–B$_4$C (batch B) and C-nano SiC–B$_4$C (batch D) developed with pitch-coated GC of dimensions 12 mm × 3 mm × 4 mm were cut and polished and the oxidation resistance studies of these weighed samples were carried out at 800, 1,000 and 1,200 °C for 5–10 h by heating them upto the required temperature in argon and by changing the argon atmosphere to air atmosphere for the specified period followed by weighing them after cooling to RT. The surface morphology of C-micro or nano SiC–B$_4$C composites developed by using pitch-coated GC (batches B and D) and of C-nano SiC–B$_4$C composite (batch D) oxidized at 800 °C was determined by scanning electron microscopy (SEM, LEO–440).

## Results and discussion

The properties of carbon monolith derived from GC as such and from the pitch-coated GC by heat treatment at 1,400 °C in nitrogen were determined at RT and are given in Table 1. It is seen from the values in Table 1 that the bulk density of carbon monolith derived from the coated GC is higher as compared to the carbon monolith derived from uncoated GC, i.e. density values increased on heat treatment to 1,000 and 1,400 °C from 1.69 to 1.75 gm/cm$^3$ and from 1.80 to 1.87 gm/cm$^3$ for GC and coated GC-based carbon monolith, respectively. This in turn led to significant increase in bending strength from 102 MPa for GC-derived monolithic carbon to 125 MPa for carbon monolith developed from pitch-coated GC (1,400 °C HTT). The enhancement noticed in density and the bending strength of the carbon monolith plates could be attributed to the improved binding of the self sintering GC powder by the pitch coating as high $\beta$-resin in the pitch is known to provide strength in the carbon product.

The characteristics of the C-micro SiC–B$_4$C and C-nano SiC–B$_4$C developed with GC as such (batches A and C, respectively) vis-a-vis with pitch-coated GC (batches B and D, respectively) given in Table 1 were also determined at RT. The values of the all batches showed that the bulk density of the composites increased with HTT upto 1,400 °C. Further, it was found that the bulk density of the composites derived from coated GC (batches B and D) is higher as compared to the composites developed with uncoated GC (batches A and C). The increase in bulk density observed in the case of batches B and D as

**Table 1** Characteristics of green coke/pitch-coated green coke derived carbon monolith and carbon–ceramic composites developed at a heat treatment temperature of 1,400 °C[a]

| Characteristics | HTT (°C) | Carbon monolith derived from | | Composition of the carbon-ceramic composite batches (weight percentage) | | | |
|---|---|---|---|---|---|---|---|
| | | Green coke | Pitch-coated green coke | C-micro $SiC–B_4C$ | | C-nano $SiC–B_4C$ | |
| | | | | Batch A GC-Si–$B_4C$ 60-20-20 | Batch B pitch coated GC-Si–$B_4C$ 60-20-20 | Batch C GC-CB-Si–$B_4C$ 51-9-20-20 | Batch D pitch coated GC-CB-Si–$B_4C$ 51-9-20-20 |
| Bulk density ($gm/cm^3$) | RT | 1.32 | 1.32 | 1.54 | 1.55 | 1.51 | 1.57 |
| | 1,000 | 1.69 | 1.75 | 1.83 | 1.86 | 1.67 | 1.82 |
| | 1,400 | 1.80 | 1.87 | 1.86 | 1.87 | 1.72 | 1.84 |
| Weight loss (%) | 1,000 | 9.6 | 9.8 | 4.6 | 4.7 | 4.5 | 4.6 |
| | 1,400 | 10.30 | 10.6 | 5.3 | 5.4 | 4.7 | 4.8 |
| Volume Shrinkage (%) | 1,000 | 29.5 | 31.7 | 19.4 | 20.4 | 15.8 | 16.5 |
| | 1,400 | 34.3 | 37.1 | 21.3 | 21.8 | 16.7 | 17.9 |
| Electrical Resistivity (mΩ cm) | 1,000 | 3.8 | 4.4 | – | 11.7 | 12.5 | 13.1 |
| | 1,400 | 2.9 | 3.0 | 10.1 | 10.2 | 13.5 | 13.5 |
| Bending strength (MPa) | 1,400 | 102 | 125 | 125 | 140 | 60 | 147 |

[a] All the measurements were carried out at room temperature

compared to batches A and C is probably due to the binding of ingredients by the pitch during ball milling and subsequent carbonization as mentioned above. The decrease in the bulk density of the C-nano $SiC–B_4C$ composite (batch C) developed with uncoated GC is attributed to the deficiency of the binding component due to the presence of fine CB powder in the mixture. The significant increase in the green and bulk density of composite batch D over that of batch C in spite of the addition of fine CB powder might again be due to the enhanced binding of the ingredients by the pitch as already mentioned.

The weight loss observed in all the batches (Table 1) on heat treatment upto 1,400 °C is due to the loss of volatile matters from GC as well as coated GC upto 1,400 °C. The values shown in Table 1 for batches A and B or C and D indicated that there was an insignificant increase in the weight loss and this was expected since the pitch used for coating was only around 2% (by weight).

The volume shrinkage of the heat treated carbon monolith or composite plates was mainly due to self sintering property of the GC and the values of the volume shrinkage had decreased in the carbon–ceramic composites (all batches) compared to pure carbon monolith, which might be due to reduced quantity of the GC employed for the development of these composites. The values of the volume shrinkage slightly increased for composites developed using coated GC (batch B) as compared to uncoated precursor (batch A), which could be attributed to presence of pitch in coated GC. The same trend was noticed in the batches C and D with the exception that the values of volume shrinkage were significantly reduced compared to the batches A and B, which might be attributed to addition of fine CB in the precursor composites mixture.

The values for the bending strength of the composites given in (Table 1) showed a moderate increase in the case of C-micro $SiC–B_4C$ composites (from 125 MPa for batch A to 140 MPa for batch B) while remarkable increase was observed in the case of C-nano $SiC–B_4C$ composites (batches C and D) developed with pitch-coated GC (from 60 to 147 MPa). This was also attributed to the increase in the binding of the composites achieved by coating the GC with the pitch (containing $\beta$-resins). However, significant fall in bending strength (60 MPa) of C-nano $SiC–B_4C$ (batch C) developed with GC as such, CB, Si and $B_4C$ as compared to 125 MPa for C-micro $SiC–B_4C$ (batch A) developed with same GC, Si and $B_4C$ may be attributed to the presence of fine CB in the composition (batch C), which resulted in the deficiency of binder component in the composite. The coating of GC thus, significantly improved the bending strength (batch D), i.e. 60–140 MPa due to the enhanced binding of the ingredients of the composites by the pitch whose low surface energy helped in wetting with other constituents. The pitch coating of GC melts during carbonization and bonds with constituents of carbon–ceramic composites [9].

The values of electrical resistivity exhibit slight increase by coating the GC in the carbon monolith as well as in the composites (batches A–D). However, the values of electrical resistivity are significantly higher for the carbon–ceramic composites compared to the carbon monolith, which could be attributed to the presence of high resistivity ceramic components in the carbon–ceramic composites.

## X-ray analysis

The X-ray powder pattern of the C-micro SiC–$B_4C$ and C-nano SiC–$B_4C$ composites developed with pitch-coated GC (batches B and D) are given in Fig. 1a, b. The characteristics peaks of $\beta$-SiC are seen at $2\theta = 35.7°$, 60° and 72° thereby showing that $\beta$-SiC was formed in both the batches (Fig. 1a, b). The peak due to carbon is seen at $2\theta = 26°$ and the characteristic peaks of $B_4C$ are visible around $2\theta = 24°$, 32° and 38°. This is in agreement with our earlier results in which we reported that $\beta$-SiC is formed in the composites developed with silicon, GC and boron carbide and from silicon, GC, CB and born carbide, which did not employ any pitch coating [7, 8].

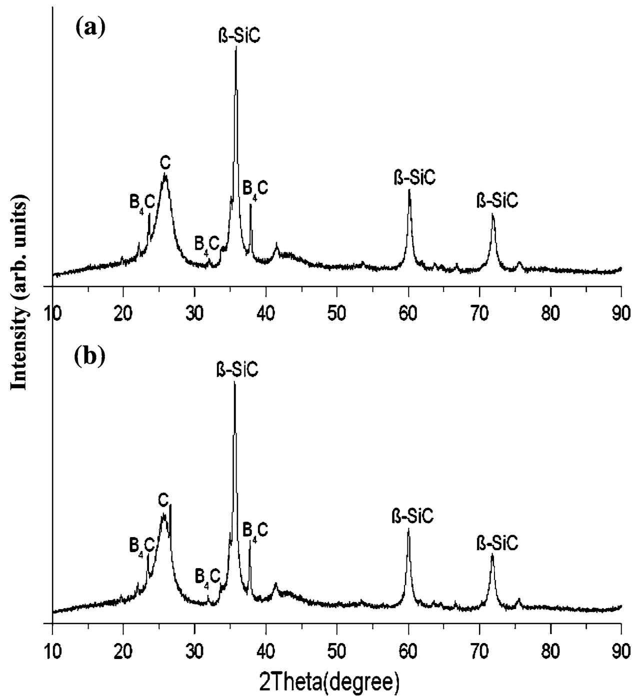

**Fig. 1** **a** X-ray diffraction pattern of C-micro SiC–$B_4C$ (batch B, developed with pitch coated green coke, HTT 1400 °C) and **b** X-ray diffraction pattern of C-nano SiC–$B_4C$ (batch D, developed with pitch-coated green coke, HTT 1,400 °C)

## Oxidation resistance studies

The weight change values on oxidation at 800, 1,000 and 1,200 °C of C-micro SiC–$B_4C$ (batch B) and C-nano SiC–$B_4C$ (batch D) composites developed with pitch-coated GC along with the values (given in parenthesis) observed for the same composites developed with uncoated GC (batches A and C) [8] are given in Table 2. It is noticed from the values that the C-micro SiC–$B_4C$ composites developed with uncoated GC (batch A) exhibited weight gain at 800–1,200 °C for 5–10 h while the C-nano SiC–$B_4C$ composite (batch C) having the same uncoated GC showed weight gain of 2.34 and 2.82% at 800 °C, 0.43 and 0.41% at 1,000 °C and weight loss of 0.61 and 0.7% at 1,200 °C for 5 and 10 h, respectively. The weight loss at 1,200 °C noticed in these composites (batch C) was attributed to the early on-start decomposition of nano SiC in air around 700 to 800 °C, which is nearly completed at 1,000 °C [8, 10–12]. Further, $B_2O_3$ formed by the oxidation of $B_4C$ in the composites started volatilizing around 900–950 °C that led to less amount of glassy boro-silicate layer formation, which provides oxidation resistance to the composites at 1,200 °C or higher [13, 14]. The weight change values observed for the C-micro SiC–$B_4C$ (batch B) composites developed with pitch-coated GC showed weight gain of 0.06 and 0.18% at 800 °C and weight loss of 0.42 and 0.28% at 1,000 °C and a weight loss of 0.49 and 0.54% at 1,200 °C for 5 and 10 h, respectively. The weight loss observed at 1,000 and 1,200 °C in C-micro SiC–$B_4C$ developed with pitch-coated GC (batch B) was due to the combined effect of silica ($SiO_2$) formation through the

**Table 2** Oxidation resistance of the carbon–ceramic composites developed at a heat treatment temperature of 1400 °C with pitch-coated green coke[a]

| Batch | Composition (in gm) | Weight change (%) after oxidation at | | |
|---|---|---|---|---|
| | | 800 °C | 1,000 °C | 1,200 °C |
| B | C-micro SiC–$B_4C$ | 0.06(5 h) [0.63*] | −0.42(5 h) [0.38*] | −0.49(5 h) [0.33*] |
| | Coated GC-Si-$B_4C$ 60-20-20 | 0.18(10 h) [0.75*] | −0.28(10 h) [0.35*] | −0.54(10 h) [0.33*] |
| D | C-nano SiC–$B_4C$ | 0.36(5 h) [2.34#] | 0.24(5 h) [0.43#] | 0.05(5 h) [−0.61#] |
| | Coated GC-CB-Si-$B_4C$ 51-9-20-20 | 0.41(10 h) [2.82#] | 0.27(10 h) [0.41#] | 0.05(10 h) [−0.70#] |

*Note*: The values given in parenthesis with * and # refer to the values for uncoated green coke based composite batches A and C, respectively, reported earlier [8]

[a] All the measurements were carried out at room temperature

oxidation of SiC in air, volatilization of $B_2O_3$ in the temperature range of 900–1,200 °C and also due to the oxidation of pitch-derived carbon. The weight loss due to the volatilization of $B_2O_3$ and oxidation of pitch-derived carbon was more than the weight gain resulting from the oxidation of SiC, which led to the formation of $SiO_2$ because micro SiC starts decomposition in air around 950 °C.

The values quoted for C-nano SiC–$B_4C$ (batch D) developed with pitch-coated GC showed weight gain at temperatures in the range 800–1,200 °C. The oxidation resistance of C-nano SiC–$B_4C$ (batch D) developed with pitch-coated GC at 800 °C (weight gain of 0.36 and 0.41% for 5 and 10 h) was due to the formation of $B_2O_3$ from $B_4C$ [13]. The oxidation resistance at 1,000–1,200 °C was attributed to the decomposition of nano SiC in air at 700–800 °C to give $SiO_2$, which compensates the weight loss due to the volatilization of $B_2O_3$ and oxidation of pitch-derived carbon. It is important to mention from our previous study [8] that nano SiC which is sensitive to oxidation exhibited a weight gain of 0.41% at 800 °C, 17.8% at 1,000 °C and 21.12% at 1,200 °C for 5 h, while micro SiC did not show any weight gain at 800 °C but exhibited only 4% weight gain at 1,000 °C for 5 h [8].

The oxidation resistance studies also revealed that the weight gain observed in the case of pitch-coated composites is always lesser that the values observed for the composites developed with GC (Table 2) as such, i.e. without coating, which was attributed to the oxidation of pitch-derived carbon resulting from the pitch-coated GC employed in these composites, which has been explained earlier and also confirmed by SEM studies discussed below.

## SEM analysis

The SEM of the composite batches B and D as such and oxidized batch D at 800 °C for 10 h are given in Figs. 2a, b and 3, respectively. The composites before oxidation showed carbon, SiC, $B_4C$ and layer of pitch-derived carbon in both the batches (Fig. 2a, b). The formation of $B_2O_3$ layers over the carbon and SiC are seen in C-nano SiC–$B_4C$, which were oxidized at 800 °C (Fig. 3). It was interesting to note that the oxidized C-nano SiC–$B_4C$ composite (batch D) showed nano SiC rods/fibres having diameter in the range of 25 to 85 nm (Fig. 3), which were not noticed in the unoxidized composite (Fig. 2b). It is important to mention here that oxidized as well as unoxidized C-nano SiC–$B_4C$ composite (batch C, without pitch coating) prepared and reported by the present authors showed the formation of SiC nano rods when viewed under SEM [8]. This difference in oxidation behaviour noticed in composites developed with GC as such and with pitch-coated GC might be due to the coating given to GC (batch D), which formed a layer of carbon over the nano SiC rods/fibres formed on heat treatment to 1,400 °C (Fig. 2b), which on oxidation got removed, thus exposing the nano rods/fibres (Fig. 3). This observation is in agreement with the result of oxidation resistance at 800 °C in which, the

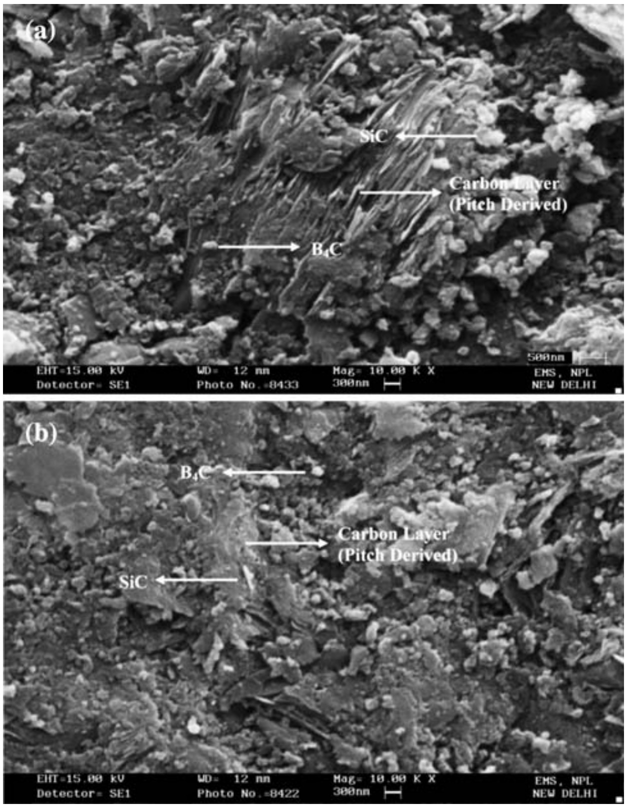

**Fig. 2** **a** SEM micrographs of C-micro SiC–$B_4C$ (batch B, developed with pitch coated green coke, HTT 1400 °C) and **b** SEM micrographs of C-nano SiC–$B_4C$ (batch D, developed with pitch coated green coke, HTT 1,400 °C)

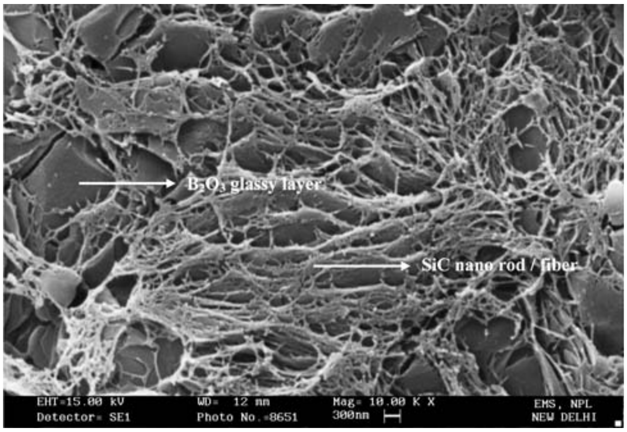

**Fig. 3** SEM micrographs of oxidized (800 °C) C-nano SiC–$B_4C$ (batch D, developed with pitch coated green coke, HTT 1,400 °C)

weight gain noticed in the pitch-coated sample is less than the weight gain observed with composites developed without providing pitch coating to GC [8]. This may be attributed to the carbon coating on the constituents formed by the melting of the pitch on heat treatment [9] and its removal during oxidation. Further, it appears that the reactivity of pitch-derived coke is lesser then that of GC and CB and therefore the carbon-derived from pitch remained intact (Fig. 2a, b) and gets removed when oxidized in air (Fig. 3).

## Conclusions

The present investigation showed that coating the precursor GC with pitch, enhanced the physical and mechanical properties of the carbon–ceramic composites (micro and nano) without affecting significantly their oxidation resistance. The coated C-micro SiC–$B_4C$ showed slight weight gain at 800 °C and negligible weight loss at 1,000 and 1,200 °C while C-nano SiC–$B_4C$ always exhibited weight gain at 800–1,200 °C. The weight gain observed during oxidation in these carbon–ceramic composites developed with pitch coating was found to be less than the composites developed without pitch coating. The nano composites developed with coated GC exhibited improved oxidation resistance and mechanical properties compared to that of uncoated carbon–ceramic composites.

**Acknowledgement** The authors are thankful to Dr. Vikram Kumar, Director for his kind permission to publish these results and to Dr. A. K. Gupta for the encouragement throughout the investigation. Thanks are also due to Dr. V. P. S. Awana and Mr. K.·N. Sood for their help in X-ray and SEM measurements, respectively. The authors are also thankful to Department of Science and Technology New Delhi for sanctioning the project on carbon–ceramic composites and also for the grant of project assistanceship to Mr. Rajeev Kumar, Mr. Sandeep Kumar and Mr. Anil Kumar.

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