CHAPTER III

EFFECT OF BORON CARBIDE (ABRASIVE) ON VARIOUS PROPERTIES OF CARBON-CERAMIC COMPOSITES

Carbon-carbide-ceramic composites (CCC) were developed using powder metallurgical method which involves mixing of reinforcements i.e. silicon carbide and boron carbide with thermosetting resin (phenolic resin) and CPC as carbon precursor. Boron carbide compositions were varied as 5, 10, 20 and 30 weight % which were named as CCC1, CCC2, CCC3 and CCC4 respectively (Table 2.2). Ball-milled powders of different composition were then hot pressed at 200 kg/m² to get green blocks. These different CCC composites were carbonized to 1000°C in inert atmosphere. Carbonized carbon-carbide-ceramic composites were analyzed for their physical, tribological and mechanical properties. Also, carbonized CCC composites were heat treated to 800°C and 1000°C in presence of air to study the effect of SiO₂ and B₂O₃ layer on oxidation resistance and tribological property of the carbonized CCC composites.

3.1 Characterization of raw materials

Characterization of raw materials was done before processing of carbon-ceramic composites. Thermo-gravimetric analysis was done for phenolic resin in nitrogen atmosphere to calculated the percentage of carbon yield. Volatile content of calcined petroleum coke was found out by heating in furnace at 950°C in inert atmosphere. Silicon carbide powder was analyzed for particle size analysis (PSA) and XRD.
3.1a Phenolic Resin with 12% hardener

Pyrolysis behavior of phenolic resin was performed in N\textsubscript{2} atmosphere at 950\textdegree{}C with heating rate of 20\textdegree{}C/hr as shown in Figure 3.1. During carbonization stage, non-carbon elements in the cured resin were removed as volatiles, such as H\textsubscript{2}O, CO, CO\textsubscript{2}, H\textsubscript{2} and other gases. The reactions were due to the condensation of aromatic ribbon molecules in the cured resin and the volatilization of low molecular weight species. This is due to thermal pyrolysis of the polymer structures. This results in the shrinkage and weight loss in the cured resin. The carbon yield of the phenolic resin was found to be (~ 56.74\%) which shows it is a good precursor for the carbon-ceramic products. The color of such phenolic resin was yellow. Particle Size was analyzed through particle size distribution with different sieves viz.. 300\micron{} (50 A.S.T.M mesh), 212 \micron{} (70 A.S.T.M mesh), 150 \micron{} (100 A.S.T.M mesh), 102 \micron{} (140 A.S.T.M mesh), 75 \micron{} (200 A.S.T.M mesh), less than 75 \micron{} (less than 200 A.S.T.M mesh). Major of the particles were found to be in the range of 75 microns.

Fig 3.1:- Thermo-gravimetric analysis of phenolic resin in N\textsubscript{2} atmosphere
3.1b Calcined Petroleum Coke

During heating, there is evolution of volatiles from the coke which helps in the densification of the composites. The volatile content of the CPC was measured to be 4%.

3.1c Silicon Carbide/Boron Carbide

The particle size obtained was around 20 microns. The size of the SiC powder was reduced using Muller Mill (Darteno industry) to 1-5 micron size.

Mostly 20 micron particles were present in the powder. XRD pattern of the Silicon carbide powder showed a high intensity peak $2\theta_1=35.65^\circ$, $2\theta_2=60.07^\circ$ and $2\theta_3=71.89^\circ$ which showed the presence of $\beta$ SiC. The presence of peaks at $40^\circ$, $65^\circ$, and $90^\circ$ shows small amount of metal oxides (Figure 3.2). Table 3.1 gives the particle size of various ingredients used for processing of carbon-carbide-ceramic composites.

![XRD of Carborundum Silicon Carbide powder](image)

**Fig 3.2:** XRD of Carborundum Silicon Carbide powder

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic resin</td>
<td>60-75 microns</td>
</tr>
<tr>
<td>Calcined petroleum</td>
<td>10-20 Microns</td>
</tr>
<tr>
<td>Beta SiC</td>
<td>10 - 20 microns</td>
</tr>
<tr>
<td>Boron carbide</td>
<td>1-1.5 microns</td>
</tr>
</tbody>
</table>

**Table 3.1:** Particle Size of different ingredients used for the processing of Carbon-carbide-ceramic composites
3.2 Physical changes during carbonization

Carbonization is accompanied by physical changes such as weight loss, volume shrinkage, density and porosity variation etc. In CCC composites physical change occurs due to pyrolysis of phenolic resin. This is expected because calcined petroleum coke itself is calcined at high temperature whereas B₄C and SiC do not undergo any chemical reaction in inert atmosphere. Figure 3.3 shows the pyrolysis curves of various CCC composites. Weight percent of the CCC composites changes with percentage of phenolic resin. The main degradation in carbon-carbide-ceramic composites occurs in the temperature range 400°C to 600°C. This is due to release of main quantity of gaseous degradation products, such as water, carbon monoxide, carbon dioxide, methane, phenol, cresols and xylenols [1]. In the temperature range from 600°C to 800°C, further weight loss is observed due to the evolution of some gaseous products, such as CO, CH, benzene, phenol, cresols [1]. Figure 3.4 shows percentage change in weight and volume with variation of phenolic resin.

![Pyrolysis curves for various CCC composites with variation on phenolic resin](image)

**Fig 3.3:-** Pyrolysis curves for various CCC composites with variation on phenolic resin
3.2.1 Pyrolysis of Phenolic resin to carbon char

Pyrolysis is one of the critical processes in the manufacture of carbon or related composites with phenol-formaldehyde resin. The pyrolysis reaction converts the resin matrix into amorphous carbon. The potential damage during this process is serious because of the thermal stresses that develop in the composites and high pressures from the evolution of many gaseous products. The whole mechanism of pyrolysis can be series of both simultaneous and sequential reactions of condensation, oxidation, dehydration, decomposition, formation of additional crosslink, the scission of crosslink, and polycyclic aromatization. Figure 3.5 shows a general sequence of probable chemical reactions occurring during pyrolysis of phenol-formaldehyde polymer [2]. As shown in the figure, during pyrolysis various dissociation/condensation reactions takes place concurrently. Therefore, weight loss of the polymers during pyrolysis is accompanied by volumetric shrinkage. Matrix shrinkage has a dominating effect on the microstructure and performance of carbon based composites. Excessive shrinkage during

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**Fig 3.4:** Percentage change in weight and volume with variation of phenolic resin

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carbonization generates stresses at the reinforcement/matrix interface and often results in matrix cracks. A systematic analysis of the pyrolysis mechanism and TGA analysis of resin matrixes help in choosing optimum carbonization conditions, especially the rate of heating in particular temperature region. The solid-state pyrolysis of highly cross linked polymers results in turbostatic carbon with aromatic systems angularly displaced. These resins yield low density non-graphitizable carbons with closed porosity, which limits the density of carbon based composites [3].

The slight weight loss in first stage i.e. up to 200°C is due to the loss of moisture, and the second stage, up to 400°C, may be attributed to the loss of some volatiles, such as unreacted phenol and formaldehyde, etc.

According to the pyrolysis chemistry of PF resin, phenolic hydroxyl is active in pyrolysis, but there is no direct relationship on the decomposition of PF resin. In contrast, its reaction with methylene forms an additional crosslink in polymer chain backbone at initial pyrolysis stage, which may strengthen the thermal stability [4, 5]. Besides reacting with phenolic hydroxyl, methylene can also be oxidized or scissored out of polymer chain backbone. According to the Figure 3.3 phenol and its methyl derivatives are the main volatiles when PF resin is pyrolyzed at 450°C. This means some methylenes are scissored as the pyrolysis reactions proceed [6].

Further pyrolysis chemistry of phenol formaldehyde suggests that phenol and its methyl derivatives are always the majority volatiles whenever PF resin is pyrolyzed at 450, 550, 650 or 750°C. Therefore, it can be inferred that methylene scission results in the damage of polymer chain backbone. It should be also noted that some volatiles such as benzene and its methyl derivatives are released at temperature above 650°C. These volatiles propose that some phenolic
hydroxyls are apparently stripped off, and hydroxyl radicals are generated correspondingly. There are almost no carboxyl compounds in the pyrolysis products which can be explained by the difference in thermal stability. The carboxyl located at the terminal chain, is debonded upon the formation of carbon dioxide at high temperatures. The carbonyl located between aromatic rings, has a higher stability for the conjugation effect. It is not removed until the temperature is sufficiently high and carbon monoxide is released. Therefore, carbon dioxide evolves before carbon monoxide.

In the whole pyrolysis process, an additional crosslink is firstly formed between methylene and phenolic hydroxyl. Second, some methylene are scissored, thereby generating some volatiles including phenol and its methyl derivatives. Third, some phenolic hydroxyls are stripped off with the formation of hydroxyl radical. Hydroxyl radicals react with methylene and hydroxymethyl, leading to the release of carbon dioxide and carbon monoxide. Finally, the resin is gradually transformed into amorphous carbon by polycyclic reactions including those of polyaromatics.
Fig 3.5: Pyrolysis chemistry of Phenol-formaldehyde polymer

3.2.2 Density and Porosity of CCC composites

Density and kerosene porosity of green and carbonized CCC composites were measured. These are plotted in figure 3.6. It is seen from figure 3.6 that the density of the CCC composites increases with the heat treatment temperature. The densities of green CCC composites were measured as 1.64 g/cm$^3$, 1.68 g/cm$^3$, 1.75 g/cm$^3$ and 1.78 g/cm$^3$ for CCC1, CCC2, CCC3 and CCC4 respectively. In case of carbonized CCC composites it is clear that density is increased with B$_4$C amount. This is because of shrinkage in matrix (phenolic based carbon) during carbonization (heating) and reinforcements (SiC, B$_4$C) get compacted in the carbon matrix to increase in the density at 1000$^\circ$C. There is large difference in increase in density in case of CCC4 composites which is due to presence of more of amount of total ceramic content in CCC composites. CCC1 has 1.84 g/cm$^3$ carbonized density whereas CCC4 has 1.94 g/cm$^3$ carbonized density. As from table 2.2 it is known that CCC1 has 25% of total ceramic content (SiC + B$_4$C) as compared to CCC4 which has 50% of total ceramic content. The particle size of B$_4$C is (1-1.5 micron) smaller than the particle size of SiC (10-20 microns). Since CCC4 has 30% of B$_4$C
which implies that during carbonization more $\text{B}_4\text{C}$ particles get compacted in the carbon matrix leading to high packing density and less porosity. Therefore, CCC4 has higher density as compared to CCC1. Also, it can be concluded that presence of boron carbide as a secondary reinforcement seems to improve density of CCC composites.

![Graph showing change in density in CCC composites heat treated to 1000°C](image)

**Fig 3.6**: Change in density in CCC composites heat treated to 1000°C

### 3.3 Microstructural study

Microstructural analysis was done to study the microstructural changes as well as morphology for different CCC composites heat treated to 1000°C. Both matrix as well as reinforcing agents (SiC, $\text{B}_4\text{C}$) was observed under optical microscopy and SEM.

#### 3.3.1 Optical micrograph

The Optical Microscope micrograph illustrates the microstructures of CCC composites with 5% and 20% weight fraction of SiC and $\text{B}_4\text{C}$ at 50X magnification (Figure 3.7a & b). The purpose of microstructure examination was to investigate the particle size, shape morphology and distribution of the silicon carbide, boron carbide particles with their interfacial integrity between the matrix and reinforcement. The microstructure consists of three main constituents.
SiC particles are round shaped whereas B₄C particles showed hard edged like shape. The large and small dark region describes the voids present in CCC composites. Remaining regions shows presence of carbon matrix. As the percentage of B₄C particles increases dispersion of reinforcement (B₄C particles) with carbon matrix becomes more homogeneous. The particle size of SiC and B₄C powder seen in Figure 3.7 (a) and 3.7 (b) is 5-10 microns and 1-1.5 microns respectively.

![Optical micrograph of CCC composites heat treated to 1000°C](image)

**Fig 3.7:** Optical micrograph of CCC composites heat treated to 1000°C (a) CCC1 with 5 % of B₄C particles and (b) CCC 3 with 20 % B₄C particles
3.3.2 SEM

The microstructure, as revealed by scanning electron microscopy (SEM), is shown in Figure 3.8 for the CCC2 composite heat treated at 1000°C. SEM images were obtained to understand the matrix-reinforcement interactions. The dark regions are the carbon matrix whereas the black regions are pores. Observation of the composite containing both SiC and B$_4$C particles failed to distinguish between B$_4$C particles and the carbon matrix, because boron and carbon are close in atomic weight. These micrographs confirm that there was uniform distribution of B$_4$C particles in the base matrix and it clearly shows that there were less voids and discontinuities. Also, CCC2 composite has proper distribution of irregular shape particles. The micro-porosity does not alter at different places of the CCC composites. SiC and B$_4$C particles remain entrapped in the structure of the carbon matrix. A high level of the bonding between carbon matrix and reinforcement (SiC and B$_4$C particles) may be achieved during mechanochemical mixing and carbonization process.

![SEM images of CCC2 composite](image)

**Fig 3.8:** Scanning electron micrograph of CCC composites heat treated to 1000°C (CCC 2)
3.4 Mechanical properties

Mechanical properties for CCC composites were evaluated using Rockwell hardness and Compressive measurement.

3.4.1 Rockwell Hardness of CCC composites heat treated to 1000°C

The hardness of the CCC composites was evaluated using Rockwell hardness testing machine with 100 kg load and 0.5 mm diameter steel ball indenter. The indentation time for hardness measurement was 5 seconds. Addition of SiC and B₄C particles enhances hardness, as these particles are harder than carbon matrix which renders their inherent property of hardness to soft matrix. As the amount of the boron carbide is increased the hardness of the composite is found to increase. The average hardness values of CCC1, CCC2, CCC3 and CCC4 samples were measured to be 120.6, 121.8, 122.2 and 123.9 HRL respectively (Figure 3.9). The enhancement of hardness by increasing the weight percentage of B₄C particles mainly results from the presence of extremely harder B₄C particles in the carbon matrix and higher constraint to the localized matrix deformation during indentation [7-9]. CCC composites with higher hardness could be achieved which may be due to the fact that silicon carbide and boron carbide particles act as obstacles to the motion of dislocation. Therefore, from Rockwell hardness study it is evidently indicated that 30wt% boron carbide have high Rockwell hardness value.

3.4.2 Compressive measurement

Compressions tests were carried out on rectangular specimens of CCC composites of 25mm x 15 mm x 3-5 mm dimensions. The values vary from 150 – 230 MPa, which were higher as compared to fly ash/silicon based carbon-ceramic particulate composites (CFC & CSC) and this increase is more for higher amount of boron carbide (Figure 3.10). This indicates that the
addition of boron carbide leads to improvement in the compressive strength of the CCC composites. So, improvement in the compressive strength by introducing the B₄C particles could be explained by the homogeneous distribution of the B₄C particles in carbon matrix. This homogenous distribution gets better and better with increase in B₄C particles as seen from figure 3.6. Increase in homogeneity decreases the pores present in CCC composites which finally increases the compressive strength.

![Graph](image)

**Fig 3.9:** Effect of boron carbide weight % on hardness of the CCC composites

![Graph](image)

**Fig 3.10:** Effect of the boron carbide weight % on compressive strength of the CCC composites
3.5 Tribological Measurement

Dry sliding friction and wear tests were carried out using pin-on-disc type tribometer at different parameters like sliding speed, load, sliding time and percentage of abrasive reinforcement. Wear rate and wear volume of the CCC composites were calculated from weight loss measurements. CCC1 and CCC4 composites were heat treated to 600°C and 800°C to study the effect of glassy layer on the CCC composites.

3.5.1 Effect of sliding distance on the Coefficient of friction value of CCC composites heat treated at 1000°C

Friction coefficient in early stages of the test may be affected more by surface roughness than the material properties. Figure 3.11 shows typical friction coefficient (µ) versus sliding distance curves for CCC composites under different load conditions. In general, µ increases at the beginning, reaching a peak at short sliding distances. After some time, it attains a steady state value. From graph it can be seen that for 30% B₄C (CCC4) initial friction instantaneously attains steady state behavior whereas for 10% B₄C (CCC2) small increase is seen for few seconds for 5N load condition. This can be attributed for higher percentage of carbide particle present in CCC4 as compared to CCC2.

In case of 1N load condition, during starting the value of friction coefficient is 0.261 for CCC4 which remains almost constant and increases steadily upto an average value of 0.279. For CCC2, value of friction coefficient starts with 0.187 due to the interaction of static partner with carbon matrix. Then, it starts increasing almost linearly up to 0.221 over duration of 100 seconds of testing and after that it remains constant for the rest of the experimental time. In the curves of Figure 3.11 and 3.12, it is also seen that the values of friction co-efficient increases with the increase in boron carbide percentage.
Fig 3.11: Variation in COF value with sliding distance for 5N load condition

Fig 3.12: Variation in COF value with sliding distance for 1N load condition
3.5.2 Effect of boron carbide on the COF value with different load condition

Figure 3.13 shows the effect of load on the coefficient of friction value with the content of boron carbide (temperature: 25°C, Load: 1N, 2N, and 5N, linear speed: 15cm/s, sliding distance: 200m). It is seen that coefficient of friction of CCC composites increases significantly with increasing load and also increases with the content of boron carbide which indicated that boron carbide has high coefficient of friction at high load condition. The friction coefficient for 10% boron carbide under 5N load is initially about 0.261 which decreased to 0.221 with decrease in load condition (1 N).

![Graph showing the effect of boron carbide on the COF value with variation in load condition](image)

**Fig 3.13:** Effect of boron carbide on the COF value with variation in load condition
3.5.3 Effect of linear speed on the COF value for 5N load condition

Friction test were carried at various linear speed from 4.12 cm/s to 18.98 cm/s. The graph tends to show linear behavior until 10 cm/s and then it shoots upward drastically till 19 cm/s. With increase in linear speed the exposure of boron carbide particles become more which helps in roughening of the surface. In case of CCC2, the surface roughness of composites is higher as compared to CCC1 because of presence of more abrasive particles. COF value increases with increase in linear speed (Figure 3.14). The increase of friction value may be associated with ploughing effect and because of roughening of the CCC surface. COF value may increase with higher percentage of B₄C particles with increase in linear speed.

![Effect of linear speed on the COF value for CCC composites heat treated to 1000°C](image)

**Fig 3.14:** Effect of linear speed on the COF value for CCC composites heat treated to 1000°C
3.6 Wear behavior of CCC composites

Wear is the progressive loss of material due to relative motion between surface and the contacting substance or substances [10]. The wear damage may be in the form of micro-cracks or localized plastic deformation [11]. The amount of wear in any system will, in general, depend upon the number of system factors such as the applied load, machine characteristics, sliding speed, sliding distance, the environment and the material properties [12].

**Fig 3.15:** Wear rate of CCC composites with change in boron carbide percentage

**Fig 3.16:** Wear volume of CCC composites with change in boron carbide percentage
The wear rate and wear volume decreases with the increase in boron carbide percentage. Wear rate depends on the presence of carbide phase in matrix. It is seen that from Table 3.2 there is an increase in weight after wear test was performed on CCC composites. After wear test the wear tracks were showing shiny tribolayers where plastic deformation occurred during the test, can be observed which may be due to the addition of some Cr6 layers on the surface of CCC composites. The examination of worn surfaces showed that these tribolayers get clearer with increase in boron carbide. Figure 3.15 & 3.16 explains the correlation between wear rate and percentage of boron carbide.

**Table 3.2:- Weight gain, Change in Wear loss and Wear volume of CCC composites heat treated to 1000\(^\circ\)C**

<table>
<thead>
<tr>
<th>Batch</th>
<th>Composition</th>
<th>Weight gain</th>
<th>Wear Volume</th>
<th>Wear rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PF-CPC-SiC-B(_4)C</td>
<td>(%)</td>
<td>cm(^3) (x10(^{-3}))</td>
<td>m(^3)/m (x10(^{-13}))</td>
</tr>
<tr>
<td>CCC 1</td>
<td>50-25 - 20 – 5</td>
<td>1.1x10(^{-3})</td>
<td>24.3</td>
<td>0.486</td>
</tr>
<tr>
<td>CCC 2</td>
<td>50-20 - 20 –10</td>
<td>1.9 x10(^{-3})</td>
<td>21.3</td>
<td>0.426</td>
</tr>
<tr>
<td>CCC 3</td>
<td>30-30 - 20 –20</td>
<td>2.7 x10(^{-3})</td>
<td>12.89</td>
<td>0.2578</td>
</tr>
<tr>
<td>CCC 4</td>
<td>30-20 - 20 –30</td>
<td>3.7 x10(^{-3})</td>
<td>5.85</td>
<td>0.117</td>
</tr>
</tbody>
</table>

In the present study, the abrupt increase in COF as shown in Figure 3.11 accompanied with decrease in wear rate may correspond to wear mechanism from a mainly abrasive wear to a combination of adhesive wear, abrasive wear as shown in Figure 3.17.

During friction test initially there was loss of material in form of wear debris which may be due to gouging and ploughing of abrasive particles. Slowly, as the sliding time and sliding distance local pressure at the asperities become extremely high resulting in adhesive wear. The asperities deform plastically until the real area of contact has increased sufficiently to support the applied load. An adhesive tribolayers of shiny appearance occurs on the surface of the CCC.
composites. This layer can be associated with the continuous rubbing of Cr6 ball (static partner) on CCC surface.

![Diagram of abrasive and adhesive wear](image)

**Fig 3.17:** A schematic of abrasive and adhesive wear occurring in various CCC composites

### 3.7 Worn surface of CCC composites heat treated to 1000°C

Figure 3.18(a-d) shows worn surfaces of carbon-carbide-ceramic composites heat treated to 1000°C with 5N load condition, 2000mm sliding distance and 15.69cm/s linear speed for CCC1 and CCC4. It can be concluded from the figure that the surface obtained after friction test for CCC1 have almost smooth surface. The crack formation on surface is less. In case of CCC4 these surfaces tend to get delaminated i.e. extensive delamination of compacted surface layer in the form of flakes occurs. This may be due to higher content of boron carbide in CCC4 which have rhombohedral structure which does not allow to form a smooth layer. The worn surface in a slightly higher magnification (Fig. 3.18c & d) reveals the compacted smooth plateau with the locally detached regions with fell apart ingredients, supporting the abrasive wear mechanism.
Fig 3.18 (a-d):- Worn surfaces of carbon-carbide composites (CCC1 and CCC4) heat treated to 1000°C
3.8 Friction property of CCC composites after heating in presence of air to 800°C and 1000°C

Many applications of braking materials require extended periods of performance ranging from a few hours (at high temperature) to a few thousands of hours (at low temperature) in oxidizing environments where unprotected composites deteriorate rapidly. Although the oxidation behavior of SiC and B₄C composites has been investigated for many years, the effect of oxidation mechanisms on friction properties of SiC–B₄C composites have not yet been well studied. Therefore, an attempt has been conducted to study their friction property against oxidizing environment and effect of SiO₂–B₂O₃ layer on CCC composites.

Boron carbide has been used for various engineering materials such as wear parts and abrasives because of its high hardness and excellent wear resistance. The study of oxidation resistance of boron carbide is an important issue for its practical applications at high temperatures. The oxidation behavior has been reported by several research groups [13–19]. Liquid B₂O₃ was detected as the oxidation product. The liquid B₂O₃ layer cannot effectively protect boron carbide because of its low viscosity and high vapor pressure at high temperatures [170]. It is well known that presence of SiC during oxidation provides excellent protective layer. Therefore a combination of both ceramics can provide good oxidation as well as wear properties.

3.8.1 Mass and Density change during oxidation of CCC composites

Oxidation tests of the CCC composites were carried out at temperature of 800°C and 1000°C with hold time of 2 hours. This results in weight change and density change in CCC composites. When the CCC composite is exposed to high temperature in air, SiC and B₄C are oxidized to form SiO₂ [20] and B₂O₃ [21] layer depending on the composition of SiC-B₄C. In case of CCC 1, a small amount of boron oxide obtained from B₄C additives would exert a
marked inhibiting effect by blocking the active sites of carbon substrates [22,23] lowering the oxidation rate whereas on the other hand CCC 4 have large amount of B\textsubscript{4}C which further reduces oxidation rate.

**Table 3.3:- Oxidation resistance of carbon- carbide-ceramic composites**

<table>
<thead>
<tr>
<th>Batch</th>
<th>Composition</th>
<th>Weight Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PF-CPC-SiC-B\textsubscript{4}C</td>
<td>800°C (2h)</td>
</tr>
<tr>
<td>CCC 1</td>
<td>50- 25 - 20 – 5</td>
<td>1.437</td>
</tr>
<tr>
<td>CCC 4</td>
<td>30- 20 - 20 – 30</td>
<td>0.184</td>
</tr>
</tbody>
</table>

Table 3.3 illustrates the weight changes of CCC composites oxidized at 800°C and 1000°C. At this temperature, change in samples weight is minimum for 2 hour hold time. It indicates that the oxidizing products of SiC and B\textsubscript{4}C form an effective protective film to resist further oxidation. Oxidation protection becomes much effective with the increase of the B\textsubscript{4}C content in the CCC composites, so the weight loss is decreased at the same time with formation of more B\textsubscript{2}O\textsubscript{3} layer.

The slight weight loss in CCC composites is because of oxidation of carbon substrates at some unprotected active sites only exposed to the oxidative atmosphere. The presence of boron changed the active edge atoms of the planar layer into non-active ones, which would lower the oxidation rate. During oxidation at 800°C, the CCC composites showed an apparent weight-change during 2 hour duration. With increase of temperature, B2O3 layer would be formed due to oxidation of B\textsubscript{4}C additives. At this period of oxidation time, carbon substrates at the surface of the composites were oxidized to form boron oxide layer from B\textsubscript{4}C additives, [24] in case of CCC composites oxidized to 1000°C. Although the formation of B\textsubscript{2}O\textsubscript{3} could lead to mass gain theoretically, the oxidation rate may be still large due to fact that carbon consumption with mass
loss was predominant. When the temperature rose to above 700°C, though the oxidation of B₄C occurred most rapidly [25] but the oxidation rate of CCC 1 composites is also found to increase. This may be due to volatilization of boron oxide and deterioration of the boron oxide film and consequent disability to effectively prevent oxygen from diffusing into the interior of the composites at high temperature. When the temperature is higher than 800°C in case of CCC 4, the oxidation rate of CCC composites further decreased due to the formation of SiO₂ layer from SiC additives, which formed borosilicate glass as SiO₂ dissolved into B₂O₃. The rate of oxidation of composite CCC 4 was controlled by the diffusion rate of oxygen through the boron oxide film and the interstices between boron oxide and SiC additives [26].

Figure 3.19 shows change in density with oxidation temperature. There is slight decrease in density at 800°C and then increase in density after 800°C. During oxidation, carbon substrates are exposed to oxygen environment which allows carbon layer to deteriorate leading to the formation of pits. Meanwhile also, formation of B₂O₃ occurs. For CCC 1, due to lower content of B₄C it was difficult for boron oxide to fill up all the pits occurred during oxidation of carbon substrates. CCC 4 composite have higher B₄C content and the highest B₄C/SiC ratio which forms enough boron oxide and is filled up by the pits created during oxidation of carbon substrates at 800°C. Therefore CCC 4 composites which are composed of boron oxide and SiC additives had few voids or pits and slightly higher density.
3.8.2 Effect of SiO$_2$-B$_2$O$_3$ layer on friction value of CCC composites

CCC composites were oxidized to 800$^\circ$C and 1000$^\circ$C which resulted in formation of SiO$_2$-B$_2$O$_3$ layer. This changes the friction value of the composites. These oxidized CCC composites were tested for their friction value at 5N load condition, linear speed of 15.69 cm/s and a sliding distance of 2000 m. Figure 3.20 a-d, denote the variation of the friction coefficients of the samples as a function of sliding time. It is seen that initially friction curve sows steep decrease which then starts increasing substantially with sliding time and distance and reach values of about 0.332 and 0.419 for CCC 1 and CCC 4 oxidized to 800$^\circ$C. The protective B$_2$O$_3$ oxide layer tends to break down because of low oxidizing temperature and low density. As, the oxidation temperature increases there is formation of hard glassy SiO$_2$-B$_2$O$_3$ layer which increases the friction value for CCC composites oxidized to 1000$^\circ$C.
Fig 3.20a:- Friction value of CCC 1 composite after oxidation to 800°C (COF -0.332)

Fig 3.20b:- Friction value of CCC 4 composite after oxidation to 800°C (COF -0.419)

Fig 3.20c:- Friction value of CCC 1 composite after oxidation to 1000°C (COF -0.472)

Fig 3.20d:- Friction value of CCC 4 composite after oxidation to 1000°C (COF -0.544)
Figure 3.21 shows the effect of oxidation temperature on COF value during oxidation of CCC composites. As seen from the friction curves there is increase in friction value with increase in oxidation temperature. For CCC 1 composites oxidized to 800°C B₂O₃ oxide layer is very thin but for CCC 4 composites in addition to B₂O₃ oxide layer there is also SiO₂ glassy layer which increases the friction value. In case of CCC composites oxidized to 1000°C this SiO₂ - B₂O₃ layer becomes more effective and hard which further increases COF value.
References