CHAPTER 6

FIBER REINFORCED CARBON
AND CARBON-CERAMIC
COMPOSITES THROUGH SELF
SINTERABLE ROUTE
6.1 INTRODUCTION:

After having studied the development of solid carbon products from self sinterable coke powder discussed in chapter 4, ceramics were added to this carbon, producing another class of particulate composites, called carbon ceramic composites. These composites show good oxidation resistance and good mechanical properties and physical properties. These composites show good graphitizability even at low temperature because of addition of ceramics, boron carbide. But the failure of these composites was still observed to be catastrophic. They are brittle.

In order to improve the structural properties, fibrous reinforcements were incorporated. Since the objective in the present studies was to develop a low cost technique for making carbon-carbon composites, high strength carbon fibers were used as reinforcement with sinterable carbon discussed above as the matrix. Presently, efforts are going on to develop low cost general purpose carbon/carbon composites using alternative fibers such as oxidized PAN fibers as reinforcement. Therefore in the present studies oxidized PAN fibers was also used as reinforcement to make carbon/carbon composites with sinterable carbon as matrix. The two reinforcing fibers showed different behavior during sintering of the composites.

6.2 FIBER REINFORCED CARBON MATRIX (GREEN) COMPOSITES MADE FROM SELF SINTERABLE COKE:

Carbon fibers as well as oxidized PAN fibers were cut in short form (1-5 mm Length). These were than separately added to sinterable coke with optimum grinding time. The mixed was further co-milled for different times. The mixed after co-grinding was uniaxially compressed at room temperature under different pressures. Effect of all these variables on compactness of the samples was studied taking density as the criteria.
Fig. 6.3 Effect of fiber addition on ultimate linear shrinkage and weight loss during sintering of carbon-carbon composites
composites made with 30% PANOX fibers show higher weight loss than those made with 10% PANOX fibers.

6.4 SINTERING OF FIBER REINFORCED CARBON MATRIX COMPOSITES:

Addition of fibers has marked effect on the density of sintered composites.

Fig. 6.4. shows variation of density of sintered composites with co-grinding time. Density of green composites is also included for comparison. As discussed earlier, the density of green composites increases with co-grinding time. The density of sintered composites also increase with co-grinding time. But the increase in density in sintered composites is much higher than that in green composites. It supports the hypothesis that with increased co-grinding time, the fiber is also getting more and more fine with coke sticking on it. This when compressed leads to dense products. These dense products during sintering show more shrinkage (as also evident from the Fig.) and higher sintered density.

Fig. 6.5. shows variation in density of sintered products with addition of fibers. With addition of carbon fibers, the density increase. This is due to higher density of carbon fiber itself as compared to that of raw coke or sintered coke. The increase in density is not observed to be quite proportional to the amount of fibers added. This is because of the generation of more and more cracks and voids in the composites.

With addition of oxidized PAN fibers, the increase in density is found to follow the same pattern as that for green composites. The density of sintered composites also increases with increase in fiber contents up to 30%. With more addition of fibers, the density of sintered composite shows decreasing trend. In case of oxidized PAN fiber addition, the composites show shrinkage and weight loss during sintering (Fig. 6.6). The two are linear up to fiber volume addition of 30%. With higher fiber loading, the shrinkage is observed to decrease where the weight
Fig. 6.6 Effect of Fiber concentration on weight loss and linear shrinkage during sintering to 1000°C
loss continues. The weight loss is an independent phenomenon whereas shrinkage depends on the compaction at the green stage. Since with fiber loading more than 30%, the compaction at the green stage is not good the net shrinkage decreases. Additional voids and cracks are introduced during sintering. These combined with weight loss result in decrease in density of the sintered composites having fiber content more than 30%.

Therefore, these studies show that with addition of 30% oxidized PAN fibers into sinterable coke and co-grinding for 60 hrs. Result in highly compacted green composites and highly dense sintered composites.

6.4.1 HIGH TEMPERATURE HEAT TREATMENT OF OXIDIZED PAN FIBERS REINFORCED CARBON COMPOSITES:

Composites made with different amount of oxidized PAN fibers were heat treated to 2000°C and above. The change in weight, volume and density during high temperature heat treatment are compiled in Table 6.1. As seen from the table 6.1, during sintering to 2000°C and above, there is further weight loss of 3-5%. The composites exhibit volume shrinkage of 10 to 16%. Again composites made with 30% OXPAN fibers exhibit maximum changes and result in highly dense composites. It shows that the factors responsible for increase in density in the green stage and sintered stage are carried on to high temperature heat treatment stage.
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<th>CONTENT</th>
<th>HTT°C</th>
<th>Density (gm./cc)</th>
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<th>Volume shrinkage (%)</th>
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<td>1.46</td>
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Table 6.1: Change in density, weight loss and volume shrinkage during high temperature heat treatment.
6.4.2 POROSITY OF CARBON-CARBON COMPOSITES SINTERED AT DIFFERENT TEMPERATURES:

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<th>HTT °C</th>
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</table>

Table 6.2: Porosity of carbon-carbon composites treated at different temperatures and the role of ceramic addition.

Table 6.2 shows porosity of composites made with varying fiber concentration. Some characteristics have been observed, that porosity is dependence on density of the product. Composites made with 30% oxidized PAN fibers have low porosity, the reason is it has highest density. These composites have more porosity, because no chemical bonding exist between fibers and matrix at green stage. Therefore during sintering, the fibers shrink away from the matrix leading to a small gap between fiber and matrix. This can be observed under optical microscope. Porosity increases with treatment temperature.

With addition of Silicon carbide in these composites, porosity still increases with treatment temperature. But with addition of Boron carbide along with Silicon carbide, porosity decreases. Because boron diffuse at the substitutional position of carbon atoms. Also boron carbide improve the graphitizability and the composites graphitize even at lower temperature. This can be evident with XRD studies.
6.5 MICROSTRUCTURE OF CARBON-CARBON COMPOSITES AND THE ROLE OF CERAMIC ADDITION:

6.5.1 SEM AND OPTICAL MICROSCOPY:

Fig. 6.7 shows optical micrograph of carbon fiber reinforced carbon (green) composites. At places it shows good bonding between carbon fiber and coke and at places the bonding is weak. On carbonization i.e. sintering to 1000°C, lot of cracks are developed. Fig. 6.8a and Fig. 6.8b shows optical micrograph of the sintered composite. As seen in figure 6.8 a&b, the coke powder gets sintered and densified leaving behind big voids.

Fig. 6.9 shows SEM micrograph of fractured sintered composite made with carbon fiber. It shows fiber pull out characteristic in the composite and the voids.

Fig. 6.10 Shows optical micrograph of PANOX fiber reinforced sinterable coke (green) composites. As seen from the Fig., the fibers are uniformly distributed in the carbon matrix. PANOX fibers have reactive groups on the surface. Therefore, when the PANOX fibers are co-milled with sinterable coke, the powder gets stuck on the surface of the fibers. This is seen in Fig. 6.11 Which is the optical micrograph of PANOX fiber reinforced sinterable coke (green) composites. Even on sintering, the coke remains adhered on to the surface of the fibers (Fig.6.12). On removing coke powder from the surface of the fiber through polishing, very interesting results are revealed. Fig.6.13 shows optical micrograph under polarized light of sintered PANOX fiber reinforced coke composites sintered to different temperatures. As seen in Fig. 6.13a, the fibers starts exhibiting anisotropic structure even at 1000°C. On heat treatment to 2000°C, the anisotropic texture in the fiber gets enhanced (Fig. 6.13b) and at 2700°C, the fibers exhibit highly anisotropic transverse texture (Fig.6.13c). The PANOX fibers maintain their character even after heat treatment of the composites to 2700°C. On fracture, the composites exhibit pseudoplastic fracture with fiber pullout (Fig. 6.14). However, unlike carbon fibers, carbon matrix of the composites is well adhered to PANOX fibers. The fiber
Fig. 6.7: Optical micrograph of carbon fiber reinforced carbon (green) composite.

Fig. 6.8a: Optical micrograph of sintered carbon fiber reinforced carbon composite.
Fig. 6.8b: Optical micrograph of sintered carbon fiber reinforced carbon composite.

Fig. 6.9: SEM micrograph of fractured sintered carbon fiber reinforced carbon composite.
Fig. 6.10: Optical micrograph of PANOX fiber reinforced sinterable coke (green) composite.
Fig. 6.11: Optical micrograph of PANOX fiber reinforced sinterable coke (green) composite

Fig. 6.12: Optical micrograph of PANOX fiber reinforced sinterable coke (green) composite
Fig. 6.13: Optical micrograph under polarized light of PAN OX fiber reinforced coke composite (sintered)
matrix bonding is also quite strong (Fig. 6.14b). This fiber-matrix bonding is of medium type and hence imparts strength to the composites with pseudoplastic fracture characteristic. Fig.6.15 shows SEM micrographs of PANOX fiber reinforced carbon-ceramic composites sintered at different temperatures. It shows similar characteristics as those seen in PANOX fiber reinforced carbon matrix composites sintered to these temperatures except that the matrix is a mixed carbon-silicon carbide matrix.

Addition of Boron carbide has marked effect on the matrix characteristics. Fig.6.16 shows SEM micrographs of PANOX reinforced (carbon+silicon carbide+boron carbide) matrix composites heated to 2000°C. The development of highly crystalline texture in the matrix, characteristic of boron carbide addition is seen in these figures.

6.5.2 XRD STUDIES ON CARBON-CARBON COMPOSITES AND THE EFFECT OF CERAMIC ADDITION ON THE STRUCTURE OF CARBON-CARBON COMPOSITES:

Fig.6.17 shows XRD pattern of PANOX reinforced carbon matrix composites heat treated to 2400°C. It does not show any broad band. But it shows highly intense sharp peaks. Finger printing of the peaks present in the Fig.6.17 with those of graphite, silicon carbide and boron carbide suggests that it contains all the peaks corresponding to graphite, silicon carbide and boron carbide. The figure shows that the material is highly graphitized. It shows characteristic peaks at 2θ =26.3° corresponding to 002 planes. The d₀₀₂ spacing is 0.3378 nm, very close to 0.335 nm for highly oriented pyrolytic graphite. This also shows characteristic doublet at 2θ =42° and sharp peaks at 2θ =54.3° corresponding to 004 planes, at 2θ =77.7° corresponding to 110 planes and 2θ =84° corresponding to 112 planes. PANOX fibers as such are non graphitizable carbons and when heated to 2400°C do not exhibit strong crystalline nature. But when co-carbonized with sinterable coke
Fig. 6.14: SEM micrograph of PANOX fiber reinforced coke composite showing fiber pull out.
Fig. 6.15: SEM micrograph of PANOX fiber reinforced carbon-ceramic composite sintered at different temperature.
Fig. 6.16: SEM micrograph of PANONX fiber reinforced (carbon+silicon carbide+boron carbide) heated treated to 2000°C.
Fig. 6.17: X-ray Diffraction pattern of PANOX reinforced carbon matrix composites heat treated to 2200° C
and heat treated to high temperatures, exhibit remarkable graphitic structure even at 2400°C. This suggests that during co-grinding some stresses get develop in the fibers and at the interface resulting in graphitization of otherwise non graphitizable fibers.

6.6 COMPOSITES MADE WITH OXIDIZED PAN FIBERS AND CERAMIC POWDERS AS ADDITIVES:

With an aim to develop hard and dense carbon based composites, fine ceramic powders of Silicon carbide and Boron carbide were added to OXPAN reinforced composites. Studies were made on the compactness and sinterability of composites with varying compositions of OXPAN and ceramic powders.

Ceramics (SiC and B₄C) were added in the raw coke and stepple fibers, then these were compressed at the pressure of 450 Kg/cm². Green body of carbon/carbon fiber/ceramic was obtained. These green composites were then sintered at different temperatures. These composites were characterized for physical, mechanical, electrical and thermal properties. The structural studies of these carbon ceramic composites show very interesting features. Porosity of these composites were calculated by mercury porosimetry. XRD studies were also done to see the structural change due to heat treatment. These were tested for oxidation resistance behavior.

6.6.1 DENSITY OF COMPOSITES MADE WITH OXPAN FIBERS AND CERAMIC POWDERS:

Density of the green composites made with sinterable coke, 30% SiC and varying amount of OXPAN fibers in compiled is Table 6.3. Like in section the density of the green composites is found to be maximum for composites made with 30% PANOX fibers.
Table 6.3: Effect of addition of ceramic powders on green density of carbon-carbon composites.

<table>
<thead>
<tr>
<th>Content</th>
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<td>Carbon + 20% PANOX + 30% SiC</td>
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</tr>
<tr>
<td>Carbon + 30% PANOX + 30% SiC</td>
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</tr>
<tr>
<td>Carbon + 40% PANOX + 30% SiC</td>
<td>1.398</td>
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<tr>
<td>Carbon + 50% PANOX + 30% SiC</td>
<td>1.38</td>
</tr>
<tr>
<td>Carbon + 20% PANOX + 30% SiC + 10% B₄C</td>
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<tr>
<td>Carbon + 30% PANOX + 30% SiC + 10% B₄C</td>
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6.6.2 SINTERING OF COMPOSITES MADE WITH OXPAN FIBERS AND CERAMIC POWDERS:

Fig. 6.18 shows shrinkage during sintering of fibers reinforced carbon-ceramic matrix composites with 30% PANOX fibers. This is observed to follow the same pattern as green solid carbon itself or green carbon-ceramic composites. These show expansion up to 450°C followed by shrinkage. However, the amount of initial expansion as well as net shrinkage are quite reduced. These reductions are attributed to the presence of ceramic powders in the matrix and increased porosity in the initial stages itself. Physical changes taking place during sintering of composites made with different amount of fibers are compiled in Table 6.4. Weight loss during sintering corresponds to the relative amounts of carbon and PANOX fibers in the composites. Composites made with 30% PANOX are found to possess maximum density. The Composites made with SiC and Boron carbide have good density even at low temperatures (100°C).

Table 6.5 shows physical changes during higher temperature heat treatment of the composites made with fibers and ceramics as additives to sinterable carbon.
Fig. 6.18. Shrinkage during pyrolysis of fiber reinforced Carbon Ceramic composites made with 30% PANOX
On heat treatment to higher temperatures (2200°C), the densities of the composites have been found to decrease.

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<th>Sintered Density g/cc</th>
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<th>Volume shrinkage (%)</th>
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Table 6.4: Physical changes during sintering of carbon-carbon composites made with and without ceramic additives.

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Table 6.5: Effect of high temperature treatment on the physical property of carbon-carbon composites made with ceramic powders.
Table 6.6: Compressive strength of composites made with different concentration of fibers and ceramic additives.

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6.8 RESISTIVITY OF FIBER REINFORCED CARBON MADE WITHOUT AND WITH CERAMIC ADDITIVES:

The effect on electrical resistivity with addition of fibers and additives at different temperature are compiled in table 6.7. It results in lowering the resistivity up to 30% oxidized PAN fibers, with 30% oxidized PAN fibers it is 10.63 and 12.44 mΩcm. in parallel and perpendicular direction of the compacting pressure. With increasing temperature, the resistivity decreases to 2.17 mΩcm. and 2.67 mΩcm. at 2200°C. Which is lower than the resistivity of carbon solid. This is because at high temperature the oxidized PAN fibers graphitized. With increase fiber composition beyond 30%, the resistivity increases because of porosity.
With addition of SiC in carbon-carbon composites it shows higher resistivity at 1000°C and 2200°C. This is because of complex grains of SiC in carbon matrix.

With the addition of B₄C, results shows high resistivity at 1000°C and after high temperature it yields a synergistic improvement in electrical resistivity. Because at high temperature the composites, containing B₄C and SiC will graphitized. The value of resistivity is same in both the direction of compacting pressure, which conforms the isotropic nature of the products.

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Table 6.7 : Electrical resistivity of the carbon-carbon composites heat treated at different temperatures and role of ceramic addition.
6.9 OXIDATION RESISTANCE OF CARBON-CARBON COMPOSITES AND EFFECT OF CERAMIC ADDITION:

Fig. 6.19 shows TGA curve in air of fiber reinforced carbon composites as well as those of fiber reinforced carbon-ceramic composites. Fiber reinforced composites show weight loss in air typical of carbon products, starting at 450°C and maximum in the temperature range 520-700°C. On addition of ceramic powder the oxidation resistance of the composites is found to be markedly improved. Not only the oxidation initiation temperature is found to increase but the total weight loss at 1000°C in air has also been found to reduce significantly.

<table>
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<th>Density g/cc</th>
<th>CTE X10⁴/K</th>
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Table 6.8 Effect on coefficient of thermal expansion with the addition of fibers in carbon-ceramic composites.

Table 6.8 shows the effect of addition of ceramic powder and fibers on coefficient of thermal expansion of solid carbon. It shows that the coefficient of thermal expansion decreases with addition of ceramic, this is because of the change in the structure of the carbon from polyaromatic to the graphitic. With the addition of ceramic powder porosity decreases, when the composite is heated to higher temperature. And coefficient of thermal...
Fig. 6.19. Effect of ceramic addition on oxidation resistance of carbon-carbon composites
expansion is low for the composites having low porosity i.e. composites having high density. With the addition of the fibers the value of coefficient of thermal expansion is more for the composites sintered at 1000°C. But with high temperature heat treatment, the coefficient of thermal expansion increases remarkably. This is attributed to the formation of pore at the interphase. This means the porosity increases with the heat treatment temperature. However, with the addition of ceramic the coefficient of thermal expansion reduces this is because of the reduction of the porosity. But the value is still higher than that of the composite made without fibers.