Chapter 4

EXPERIMENTAL INVESTIGATIONS

4.1 Processing of 3D C-SiC Composites: Silicon carbide matrix based composites exhibit promising thermal and mechanical properties at high temperatures and offer very good oxidation and thermal shock resistance. They are finding increasing applications in aerospace, defence and industries.

Carbon fiber reinforced SiC composites are preferred to C-C composites for oxidizing and highly erosive environment. C–SiC composites are used up to 1500°C for long durations and up to 2000°C for short durations. The main applications of C–SiC are nose tips of reusable space vehicles, leading edges of hypersonic vehicles, erosion resistant jet vanes for thrust vectoring of rocket motors and wear resistant brake materials for high speed automobiles.

Pressure less solid state sintering is possible at temperatures of 1900 – 2100°C with small amounts (<1%V) of boron and carbon dopants. However, SiC ceramics of near theoretical densities can only be produced by hot pressing, which requires temperatures approaching 2000°C, pressures greater than 30 MPa, and the use of boron carbide (1-5 V %) and aluminium (3-5 V%) dopants.

An alternative SiC bulk processing technique is reaction sintering. Reaction bonded SiC (RBSC) is developed as a nuclear fuel cladding material. This process involves the infiltration of molten
silicon into porous carbon and SiC green compact by a capillary action process. In – Situ reaction occurs between Silicon and Carbon to produce a secondary SiC phase, which then bonds the original SiC particles to produce a body of theoretical density of silicon carbide (3.2 g/cc).

The volume occupied by the newly formed silicon carbide by reaction infiltration is larger than the volume occupied by the carbon in green compact. For complete infiltration and reaction of all the carbon to occur, there must be sufficient pore volume to allow volume change. If there is insufficient pore volume in the preform, choking of pores will occur during silicon infiltration. After completion of the reaction, the excess porosity remaining within the materials is filled with molten silicon.

The mechanical and thermal properties of the fiber reinforced composites can be tailored by adjusting fiber volume fraction and fiber orientation to meet the requirements. C-SiC composites retain mechanical strength up to 1700°C and have a high thermal conductivity and low thermal expansion and hence excellent thermal shock resistance.

There are several methods to fabricate C–SiC Composites such as Chemical Vapour Infiltration (CVI), Slurry Infiltration combined with hot pressing, Polymer Infiltration Pyrolysis (PIP) etc. Among these methods, the LSI process offers many potential advantages such as single step process, low processing temperature and near net shape processing.
LSI is relatively quicker process when compared with Chemical Vapor Impregnation (CVI) and Polymer Impregnation Processes (PIP), where in a porous Carbon - Carbon composite is infiltrated with liquid silicon at 1500 – 1600°C in inert atmosphere.

These composites can be made by controlling various process parameters, such as fiber volume fraction, fiber matrix interface and the extent of conversion of molten silicon into silicon carbide which govern the mechanical properties like fracture toughness. The processing techniques for development of C-SiC are shown in Fig: 4.1.

High strength carbon fiber reinforcement in the form of woven fabric and tows are used to develop 3-D stitched perform. Low quinoline soluble coal tar pitch is used for densification of carbon fiber preform. Carborundum make SiC high purity (99% min), fine grain (4.3 – 4.5 μ) and high purity silicon metal (99% min) are other ingredients.

4.2 3D Carbon Fiber Preform Development: 3D stitched preform is the simplest case of the 3D composites development, several layers of 8 H satin carbon fabric layers are stitched together with 6000 Carbon fibers to impart third direction reinforcement (Fig: 4.2). The fiber volume fraction is worked out, taking into consideration the infiltration abilities of molten silicon vis-à-vis the thermo mechanical properties.
Fig: 4.1 Schematic Diagram for C-SiC processing from CVI, PIP, LSI Routes.
4.3 Densification process:

4.3.1 Pitch impregnation: 3D Carbon fiber preforms are infiltrated with coal tar pitch by vacuum impregnation process. Here there are two vessels as shown in Fig: 4.3. The coal tar pitch is heated to 250°C in the first vessel. Then it is impregnated into carbon fiber perform kept in the second vessel by vacuum, in inert atmosphere.

4.3.2 Carbonization: After pitch impregnation, the material is kept in the container shown in Fig: 4.4 for carbonization. This process is also called pyrolysis. In this stage, the material is heated to high temperature of 1000°C in inert atmosphere and all non-carbon material is removed. The pressure maintained in this process is approximately 1000 bar.

4.3.3 Graphitization: At this stage, the material is heated to 2600°C in inert atmosphere. The process of graphitization shown in Fig: 4.5 is done to convert amorphous carbon into graphitized carbon, which will provide relatively weak interface for reaction bonding of SiC and to improve the toughness and strength of composite. The above processes are collectively called densification. The cycle is repeated several times till we get required densification.

4.4 Siliconisation: Carbon-Carbon porous composite is kept in graphite crucible along with silicon metal under vacuum. Silicon metal melts at temperature above 1420°C. The porous Carbon-Carbon composite is infiltrated with liquid silicon metal under vacuum and high temperature (1600°C). The experimental set up of siliconisation process is shown in Fig: 4.6. The molten silicon rises
into the pores of the carbon preform by capillary action and reacts with the matrix carbon to form silicon carbide.

Fig: 4.2 The fixture of carbon fiber preform
Fig: 4.3 Coal tar pitch impregnation process
Fig: 4.4 Carbonization process
Fig: 4.5 Graphitization process
Fig: 4.6 Siliconisation process
### 4.5 Testing and characterization:

#### 4.5.1 Density Measurement:

Increase in weight after siliconisation is a measure of the extent of conversion of carbon matrix to SiC. Density of C–SiC composite is measured using Archimedes principle using equation (4.1). Density achieved is consistent in the range of 2.3 – 2.4 g / cc.

\[
\text{Density (}\rho_{\text{C-SiC}}\text{)} = \frac{W_{\text{air}}}{(W_{\text{air}} - W_{\text{water}})} \text{ g/cc} \tag{4.1}
\]

where  
- \(W_{\text{air}}\) = The Job weight (g) in air
- \(W_{\text{water}}\) = The job weight (g) in water

#### 4.5.2 Specimen preparation and test methods:

The instrument used to perform impact test is quite similar to drop weight machines. It is usually equipped with a piezoelectric or strain gauge load cell. The standard specimens are prepared with composition shown in Table 4.1.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Constituents</th>
<th>Percentage (% Vol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Carbon (Fibre)</td>
<td>40%</td>
</tr>
<tr>
<td>2</td>
<td>SiC</td>
<td>45%</td>
</tr>
<tr>
<td>3</td>
<td>Si</td>
<td>10%</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>5%</td>
</tr>
</tbody>
</table>

Table 4.1 Composition of Carbon Silicon Carbide (C-SiC)
After preparing the specimens (C-SiC) as per the required composition, they are cut into required sizes according to ASTM D256 standards (Fig: 4.7). The Izod impact tests are conducted using Fractovis drop weight instrumented impact tester acquired with a DAS 8000 WIN data acquisition system as shown in Fig: 4.8.

All dimensions are in mm

Fig: 4.7 Izod Test specimen geometry according to ASTM D 256 standards
Fig: 4.8 Two views of the Fractovis Instrumented Impact Tester
4.5.3 **Mechanical properties measurement:** Mechanical properties of the C-SiC composite materials are characterized under impact loading to get the reliable design properties at room temperature.

4.5.4 **Impact Loading:** Instrumented impact tests on notched Izod samples are conducted as per ASTM D 256 standards to determine the energy absorbing capability and dynamic fracture behavior of the composite materials. The sample sizes are 10.16 x 12.7 x 32.5 mm and the impact velocity of 3 m/s is chosen. The dynamic fracture toughness ($\alpha_k$) is calculated using equation (4.2).

$$\alpha_k = \frac{\Delta W}{bh}$$  \hspace{1cm} (4.2)

where $\Delta W$ is the absorbing energy of materials during impact processing, b and h are thickness and width of specimen respectively.

4.5.5 **Flexural Test:**

This test method covers the determination of flexural properties of continuous fiber reinforced ceramic composites in the form of rectangular bars formed directly or cut from sheets, plates or molded shapes. According to ASTM C1341 standards, a three point loading system utilizing centre loading on a simply supported beam is chosen. The specimen geometry is shown in Fig: 4.9.

The siliconised 3D C-SiC composite specimens shown in Fig: 4.10 are cut into sizes 6mm x15mm x100mm with support span
length of 100mm along principal material direction and tested for three point bend test at room temperature to get flexural strengths.

All dimensions are in mm

Fig: 4.9 Specimen geometry for flexural test as per ASTM C1341 standards
This test method applies primarily to all advanced ceramic matrix composites with continuous fiber reinforcement: one dimensional (1D), two dimensional (2D), and three dimensional (3D) continuous fiber architectures. In addition, this test method may also be used with glass matrix composites with continuous fiber reinforcement.

However, flexural strength can not be determined for those materials that do not break or fail by tension or compression in the
outer fibers. Test can be performed at ambient temperatures or at elevated temperatures. At elevated temperatures, a suitable furnace is necessary for heating and holding the specimens at the desired testing temperatures.

In this test method, the flexural stress is computed from elastic beam theory with the simplifying assumptions that the material is homogenous and linearly elastic. This is valid for composites where the principal fiber direction is coincident or transverse with the axis of the beam.

These assumptions are necessary to calculate a flexural strength value, but limit the application to comparative type testing such as used for material development, quality control and flexure specifications. Such comparative testing requires consistent and standardized test conditions, i.e., specimen geometry (thickness), strain rates, atmospheric test conditions.

Flexure tests provide information on the strength and deformation of materials under complex flexural stress conditions. In CFCCs non-linear stress-strain behavior may develop as the result of cumulative damage processes (for example, matrix cracking, matrix / fiber de-bonding, fiber fracture, de-lamination etc.) which may be influenced by testing mode, testing rate, processing effects or environmental influence.

Some of these effects may be consequences of crack growth which can be minimized by testing at sufficiently rapid rates. A CFCC material tested in flexure may fail in a verity of distinct fracture
modes, depending on the interaction of the non-uniform stress fields in the flexure specimen and the local mechanical properties.

The specimen may fail in the tension, compression, shear or in mix of different modes depending on which mode reaches the critical stress level for failure to initiate. To obtain a valid flexural strength by this test method, the material must fail in the outer fiber surface in tension or compression, rather then by shear failure.

The geometry of the specimen must be chosen so that shear stresses are kept low relative to tension and compression stresses. This is done by maintaining a high ratio between the support span (L) and the thickness or depth (d) of the specimen. This L/d ratio is generally kept at the values of greater than or equal to 16 for 3-point flexure testing following the ASTM C1341 standards. If the span to depth ratio is too low, the specimen may fail in shear.

4.5.6 Testing Machine:

The flexural specimens are tested in a properly calibrated universal testing machine (UTM) shown in Fig: 4.11 that can be operated at the constant rates of cross head motion over the range required. The system is equipped with a means for retaining the readout of the maximum load as well as the record of load verses deformation.
Fig: 4.11 Universal Testing Machine (UTM) to conduct Tensile, Flexure and Shear tests

4.5.7 Loading fixtures:

The outer loading span and the desired test geometry determine the dimensions and geometry of the loading fixture. The fixture geometry, i.e., 3-point is selected. The thickness of the specimen to be tested determines the critical out span dimension of the loading fixture. The over all dimension of the specimen and required loading
span are selected based on the specimen thickness, the desired test geometry, and the required span to depth ratio following ASTM C1341 standards.

4.5.8 Data Acquisition:

An autographic record of the applied load and the centre point deflection is obtained for the specified cross head rate. Either analog chart recorders, or digital data acquisition systems may be used for this purpose, although a digital record is recommended for ease of subsequent data analysis. Ideally an analog chart recorder or plotter should be used in conjunction with digital data acquisition system to provide an immediate record of the test as a supplement to the digital record.

4.5.9 Specimens:

Specimen width shall not exceed \( \frac{1}{4} \)th of the support span for specimens greater than 3mm in depth. The specimen shall be long enough to allow for overhang passed the outer supports of at least 5% of the support span, but in no case, less then 5mm on each end. Overhang shall be sufficient to minimize shear failures in the specimen ends and to prevent the specimen from the slipping through the supports at large centre point deflections.

4.5.10 Conducting the test:

The test temperature is determined and recorded. The data acquisition is initiated and the load application is started. The test is continued until the specimen breaks into two pieces or there is a drop
of 20% from the maximum observed load. The maximum load is recorded. After completing the test, the action of the test machine and the data acquisition system is disabled.

In addition to the location, carefully the mode of the fracture initiation and crack extension is noted. Fracture may initiate on the tensile (lower) face, on the compression (upper) face of the bar or by shear failure. The bar may fail by a sequential combination of modes. The tensile fracture crack may extend towards the neutral axis directly or may be deflected along low strength planes such as inter laminar regions.

4.5.11 Flexural Stress (σ):

When tested in flexure, a simple beam experiences maximum tensile stresses in the outer fibers and maximum compressive stresses in the inner fibers. The location of the maximum stress along the length of the beam is at the centre point for 3-point testing. Equation for calculating the flexural stress for the 3-point test is given as:

\[
\text{Flexure Stress, } \sigma = \frac{3PL}{2bd^2}
\]  

(4.3)

Where, 

\[ P = \text{Load at given point in the test (N)} \]

\[ L = \text{Support span (mm)} \]

\[ b = \text{Specimen width (mm)} \]

\[ d = \text{Specimen depth or thickness (mm)} \]
4.5.12 **Flexural Strength (σ)**:

The flexural strength is equal to the maximum stress in the outer fibers at the point of maximum load. It is calculated using the equation:

Flexural Strength, $\sigma_f = \frac{3P_U L}{2bd^2}$ \hspace{1cm} (4.4)

Where, $P_U$ = Maximum load in flexural test (N)

$L$ = Support span (mm)

$b$ = Specimen width (mm)

$d$ = Specimen depth or thickness (mm)

4.5.13 **Shear test:**

Shear strength of 3D C-SiC composites is measured by conducting a three point bend test in the same UTM. The shear strength is calculated by the following equation.

$$\tau = \frac{3P}{4bh}$$ \hspace{1cm} (4.5)

where $P$ is the fracture load (N), $b$ and $h$ are width and thickness of the specimen respectively.

4.5.14 **Tensile Testing:**

The test specimens cut into sizes 3mm x 6mm x 100mm length according to ASTM C 1275 standards (Fig:4.12) are shown in Fig. 4.13. They are fixed in the universal testing machine (UTM) shown in Fig:4.11 to conduct tensile test by choosing the tensile fixture and properly adjusting the movable jaw so as to keep the gauge length of 25mm. The tensile load ($P$) is gradually applied along principal
material direction. When the applied load reaches ultimate value, the specimen breaks catastrophically and the load falls to zero.

All dimensions are in mm

Fig: 4.12 Tensile test specimen geometry as per ASTM C1275 standards

Fig: 4.13 Tensile test specimens
The equation for calculating longitudinal strength in tension is expressed as:

$$\sigma_t = \frac{P_U}{A} \quad (4.6)$$

where \( P_U \) = Ultimate load (kN)

\( A = \) Area of cross-section perpendicular to the direction of applied load

**4.5.15 Microstructure analysis:** The siliconised composites are analyzed for microstructure. The composites show very uniform silicon infiltration throughout the body, which is shown in Fig: 4.14 (A-F).

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**Fig: 4.14 (A) Showing Un-reacted Silicon**
Fig: 4.14 (B) Showing Uniform Silicon infiltration

Fig: 4.14 (C) Showing Porosity
Fig: 4.14 (D) Showing Fiber Orientation

Fig: 4.14 (E) Showing Fiber and Matrix Distribution
There are some un-reacted silicon traces surrounding the grains of C-SiC as expected. The SEM micrograph of the acid etched composite shows porosity which indicates the removal of unreacted silicon. This is also confirmed by the weight loss of the composite, post acid treatment.

It is also observed that the concentration of silicon in the composites is more at grain boundaries and at fiber bundles. This is because of slow diffusion of silicon into C-SiC in grains and relatively low availability of carbon in the fiber bundles compared to matrix bulk.