CHAPTER II

EXPERIMENTAL WORK

Techniques used for preparation of different types of Carbon from pine wood and their conversion to biomorphic SiC, and their characterizations are described in this chapter along with the description of the instruments used.

2.1 Introduction:

In the present work, biomorphic silicon carbide was prepared by carbothermal reduction method. The carbon template was derived from pine wood and silica sol was infiltrated into it. The carbothermal reduction was carried out at 1650°C in argon atmosphere to prepare silicon carbide.

2.2 Raw materials

- Pine wood was taken from Kaillesh Pati wood industry at Anand (G.I.D.C)
- **Gas:** Nitrogen (99.98%)
  - Argon (99.99%)

Both gases were procured from Vadilal Gas Industries at Ahmadabad.

- **Other reagents:**
  1. Tetraethyl orthosilicate [TEOS, Si (OC₂H₅)₄] (98%), Aldrich Company. Germany
  2. Ethanol [C₂H₅OH] (99.5%), Baroda chemical Industries ltd. Vadodara
  3. Phenolic resin from Kemrock industry. Vadodara
2.3 Development of porous carbon template

2.3.1 Materials used

- Pine wood

2.3.2 Carbonization of Pine wood

Small species of pine wood having 45mm length, 25mm width and 18mm dimensions were placed in stainless steel (S.S) container and carbonized to 750°C for 7 hr in inert nitrogen atmosphere in an electrical heated furnace. The pyrolysis was carried out in stainless steel container. The stainless steel container had two opening for gas inlet and another for outlet gas. The stainless steel container was placed in to muffle of electrical furnace and the temperature of the furnace was controlled by temperature programmer. Figure.2.1 shows the carbonization assembly for pine wood. The heating rate of reaction was kept very slow 30°C/hr in order to get crack free carbon template. The cooling rate of reaction was 50°C/hr. High purity Nitrogen gas was used for pyrolysis of pine wood.
2.4 Activated carbon Template

2.4.1 Material used

- Crack free carbon template

2.4.2 Steam activation of carbonized pine wood

The pores of carbonized samples get clogged after carbonization. Therefore, to open the closed pores and enhance the porosity of the carbon template, steam activation was carried out. Known amount of carbonized sample was taken in quartz tube reactor having inlet and outlet opening for passing inert gas and steam. Figure 2.2 shows set up used for steam activation for activation of carbonized samples. The quartz tube reactor was placed in the electrical heating muffle furnace and heated with a heating rate of
100°C/hr using temperature programmer. The heating and cooling rates were programmed. A chromel-alumel thermocouple was used to measure temperature of the furnace. The sample was heated in nitrogen up to 750°C at heating rate of 2°C/min. At 750°C temperature, steam was passed along with for 60 minutes at a predetermined flow of steam. The samples were cooled in nitrogen atmosphere inside the furnace and up to room temperature. The sample was weighed and stored in desiccator.

Fig.2.2 Set up for steam activation
2.5 Preparation of silica sol

2.5.1 Materials used

- Tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄)
- Ethanol (C₂H₅OH)
- Acidified water pH=2

2.5.2 Preparation of silica sol by hydrolysis of TEOS

Silica–sol was prepared by hydrolysis of tetraethoxy silane, [Si(OC₂H₅)₄], with acidic water. Ethanol was used as a solvent for TEOS and H₂O. Ethanol and TEOS were mixed in a flask using magnetic stirrer. Acidic water was added drop wise in to solution of TEOS and ethanol. The hydrolysis was carried for 12hr.

2.6 Infiltration of silica sol in to porous carbon template

2.6.1 Materials used

- Carbon template
- Silica sol

2.6.2 Infiltration of silica sol

Infiltration of silica sol into carbon- template was carried out in set up shown in fig 2.3. The weighed amount of samples was placed in to the glass container fitted with air tight lid with three outlets. The temperature was measured and maintained using thermometer. Silica-sol was passed through the middle opening, while evacuation and cleaning of samples were done by using vacuum pump. The vacuum created in the
container was measured by the vacuum gauge. The weighed sample was placed in the container and heated up to 140°C for 3hr. Then the container was cool at room temperature and silica sol was allowed to pass in to porous carbon template. The samples were dried at 70°C for 12hr and 150°C for further 12 hr to remove solvents, sticking to carbon/silica composite. The impregnation and drying of the carbon template was repeated several times to increase the infiltrated silica till a constant weight were achieved.

Fig. 2.3 Schematic set up of vacuum impregnation chamber
2.7 Carbothermal reduction of C/SiO\textsubscript{2} composite

2.7.1 Materials used

- C/SiO\textsubscript{2} composites
- Ar gas

2.7.2 Carbothermal reduction

Carbothermal reduction of as carbon-silica composite was carried out in Ar atmosphere in the electrically heated furnace (fig 2.4) at 1650\textdegree C. The heating rate was maintained with 4hr hold time with heating rate of 300\textdegree C/hr. The cooling rate was programmed at 100\textdegree C/hr up to 1000\textdegree C and 300\textdegree C up to room temperature.

Fig.2.4 Agni furnace for high temperature heat treatment and Chemical vapor reaction
2.8 Preparation of Pine wood powder

2.8.1 Materials Used

- Pine wood
- Ceramic balls

2.8.2 Ball milling of pine wood

Accurately weighed small pieces of pine wood along with ceramic balls were taken and kept in ceramic jar of ball mill shown in fig2.5. The mixture was ball milled in order to get a fine powder of pine wood. The grinding was carried out for five days to get particles of uniform size.

**Fig.2.5** Ball mill used for preparation of pine wood powder
2.9 Preparation of Silica powder

2.9.1 Materials used

- Silica-Solid
- S.S Balls
- S.S Container

2.9.2 Ball milling of Silica powder

Planetary ball mill having speed 700rpm/min was used to make silica powder of uniform size (fig.2.6). The silica –solid were mixed with stainless steel ball. The solid silica ball milled in the planetary mill at a speed of 300rpm.

Fig. 2.6 Marshal Planetary ball mill
2.10 Particle size analyzer of pine wood and silica powder

The particle size distribution of pine wood and silica powder was carried out by using mechanical sieve shaker shown in fig 2.7. The shaker is filled with sieves of different mesh sizes arranged in definite manner. The wood powder and silica powder were shaken in mechanical shaker and separated into different sizes. By using this shaker, particle size distribution of the particles having 75μm could be analyzed.

Fig.2.7 Mechanical sieve shaker for particle size analysis
2.11 Preparation of Green pellets

The mixed powder of silica and wood was hot pressed by using hydraulic press as shown in fig. 2.8. The mould die was cleaned and mould release agent was applied to inner surface of die. The die was filled with mixed powder and it was placed on the hydraulic press platform followed by pressure up to 150 kg/cm². The heating was done to 130-150°C. Circular samples having 25 mm diameter and 8 mm thickness prepared on hydraulic press were called green pellets. This green pellets were heat treated at 1000°C in inert nitrogen atmosphere having slow heating rate. The arrangement of carbonization set up shown in fig 2.1. Carbonized samples were further heat treated at 1650°C in Agni furnace shown in fig 2.4.

Fig.2.8 Hydraulic press
2.12 Characterization of Carbon template and C/\textit{SiO}_2\ Composite

\textbf{2.12.1 Determination of volatile content of raw material}

Known amounts of pine wood pieces (around 10gm) were taken in silica crucible. The crucible containing the wood samples were kept in stainless steel container having inlet for passing nitrogen and outlet for removal of volatiles. The container was placed in electrically heated muffle furnace. A chromel–alumel thermocouple was used to measure temperature of furnace. CHINO KP 1000 temperature programmer/controller was used to maintain constant heating and cooling as well as constant temperature for soaking. Samples were heated to 950\textdegree C for 2hrs at a rate of 30\textdegree C/hr under nitrogen atmosphere. The samples were cooled at a rate of 60\textdegree C/hr. The samples were then removed from the container and weighed immediately. From the difference in the weight, percentage volatile content was determined.

\[
\text{% Volatile Content} = \frac{W_1 - W_2}{W_1} \times 100
\]

Where, \(W_1\) = weight of the sample before heat treatment

\(W_2\) = weight of the sample after heat treatment
2.12.2 Percentage Char yield

Char yield was calculated from the weight of raw materials (W₁) before pyrolysis and weight of char (W₂) after pyrolysis using following relation.

\[
% \text{ Char yield} = \frac{W₂}{W₁} \times 100
\]

2.12.3 Ash Content

Known amount of dried raw materials was taken in silica crucible. The sample containing crucible was placed in electrically heated muffle furnace and heated up to 950°C for 2 hours with a current of air circulation over it. This burns off all of the combustibles and drives off volatile matter. After heating crucible was removed from the furnace and allowed to cool to room temperature in desiccator. The residue was weighed again. This was the ash. It was then calculate in percentage.

\[
% \text{ Ash content} = \frac{W₂}{W₁} \times 100
\]

Where,

W₁ = Weight of sample

W₂ = Weight of residue
2.12.4 Free carbon content

Percentage free carbon content of silicon carbide ceramic was determined by a simple heat treatment technique which was carried out in air atmosphere. The weighed SiC was taken in a stainless steel container and placed in an electrical resistance heated muffle furnace. The sample was heated in the furnace up to 950°C temperature for 3 hour. The temperature of the furnace was measured using chromel-alumel thermocouple and CHINO-KP1000 temperature programmer/controller was used to maintain the temperature of the furnace. Samples were heated at a heating rate of 30°C/hour and cooled to ambient temperature at cooling rate of 60°C/hour. After heat treatment the samples were weighed accurately and volatile content can be calculated as follows.

\[
\% \text{ Free C Content} = \frac{W_1 - W_2}{W_1} \times 100
\]

Where, \( W_1 \) = weight of the sample before heat treatment

\( W_2 \) = weight of the sample after heat treatment

2.12.5 Free silica content

Silica content of silicon carbide ceramic was determined by HF leaching, as silica gets dissolved in HF. Taken exactly 1gm of SiC powder in plastic beaker and then added HF in that beaker until whole SiC powder was completely dipped in HF. Observing the
beaker for 12 hr, after that whole solution of SiC with HF was filtrated using whatman filter paper. Dry the filter paper and weighed accurately. The percentage silica content can be calculated as follow.

\[
\text{% free silica Content} = \left(\frac{W_1 - W_2}{W_1}\right) \times 100
\]

Where, \( W_1 \) = weight of the sample before adding HF

\( W_2 \) = weight of the sample after treatment of HF leaching

### 2.12.6 Shrinkage in Dimension

The reduction of dimension in principal direction i.e. axial and radial during pyrolysis was measured by measuring the axial and radial dimensions of raw materials before pyrolysis and after pyrolysis using vernier calipers. The shrinkage in principal direction i.e. axial and radial direction was calculated by using formula

\[
\text{% axial shrinkage} = \left(\frac{\text{Axial dim. before pyrolysis}-\text{Axial dim. after pyrolysis}}{\text{Axial dim. before pyrolysis}}\right) \times 100
\]

Likewise, radial shrinkage was determined by placing the data of radial dimension in place of axial dimension.
2.12.7 Density Measurements

Bulk density of the green, carbonized and biomorphic SiC was calculated by ratio of weight of solid sample to geometric volume of the sample. Geometric volume of the sample was calculated with the help of vernier calipers by measuring length, breadth and thickness of composite.

Volume of carbon substrate \((V) = l \times b \times t\)

Where

- \(l\) = length of the sample
- \(b\) = breadth of the sample
- \(t\) = thickness of the sample

Density \((D) = \frac{\text{Weight of sample (W)}}{\text{Volume of sample (V)}}\)

2.12.8 Determination of the Porosity

The kerosene pick-up method was used for determination of open porosity of pyrolysed carbon, activated carbon and SiC. Fig.2.9 shows the experimental set-up used for determination of porosity of the materials.
Chapter II

Taken a small accurately weighed piece of the sample of dimension 2cm X 1cm X 0.5 cm. The sample was placed in flask joined in to vacuum system through a stop cock shown in fig 2.9. Then sample was evacuated with the help of vacuum pump at $10^{-2}$ torr for one hour so that trapped air in the pores of sample is removed. The vacuum pump was disconnected and kerosene was allowed to flow in the flask. Kerosene enters in to the open pores of the sample. Sample was removed from the kerosene and excess of kerosene was wiped out and sample was weighed using electronic balance LIBROR AGE-220 (shimadzu co. Japan). The density of kerosene was determined by using specific gravity bottle. The porosity of sample was calculated by using following formula.

\[
\text{% Porosity} = \frac{W_{t1} - W_{t2}}{V_s \times D_k} \times 100
\]

Where

$W_{t1}$ = weight of sample before adding kerosene

$W_{t2}$ = weight of sample after adding kerosene

$V_s$ = volume of sample

$D_k$ = Density of Kerosene
Fig. 2.9 Porosity set up for determination of porosity
2.12.9 Thermogravimetric analysis

The pyrolysis behavior of the pine wood and carbonized pine wood samples were studied using thermo gravimetric analyzer using Mettler TG-50 shown in Figure 2.10

The dried sample was taken in an alumina crucible and heated at a heating rate of 5°C/min. to 950°C temperature in an inert atmosphere. High purity nitrogen gas was used as an inert gas and flow rate of the gas was maintained at 200 CC/min. The change in weight was observed against the temperature and the results were obtained in the graphical form of thermogram.

Figure 2.10 Thermogravimetric analyzer (Mettler TG -50).
2.12.10 Differential Scanning Calorimetric analysis

The gas evolutions during pyrolysis of pine wood samples were determined using Differential Scanning Calorimeter Mettler DSC-20 as shown in Figure 2.11. Around 10 mg of sample was taken in an aluminum boat and heated along with the reference empty aluminum boat. The change in heat was obtained in the form of endothermic peaks against the temperature. The sample was heated at a heating rate of 10°C/minute in an inert atmosphere of high purity nitrogen gas.

![Differential Scanning Calorimetric Analyzer (Mettler DSC 20)](image)

**Figure 2.11** Differential Scanning Calorimetric Analyzer (Mettler DSC 20).
2.12.11 Nitrogen adsorption studies

The characteristic surface properties of carbonized and activated carbon templates were determined by nitrogen adsorption technique using Micromeritics Gemini 2375 surface area analyzer shown in Figure 2.12. The adsorption of nitrogen gas onto the activated carbon samples was studied at liquid nitrogen temperature (77 K). Prior to adsorption, samples were degassed at temperature up to 250°C in presence of inert gas argon. The samples were degassed initially at 90°C for one hour and then at 250°C for overnight (14-15 hours). After degassing the sample was weighed and attached to the surface area analyzer instrument and nitrogen adsorption studies were carried out. The amount of nitrogen gas adsorbed by activated carbon with respect to relative pressure (p/p₀) was obtained in a graphical form called adsorption isotherm. From this adsorption isotherm, the BET surface area, micropore surface area, micropore volume, total pore volume and average pore diameter were obtained.

Figure 2.12 BET Surface Area Analyzer (Micromeritics Gemini 2375).
2.12.12 Scanning Electron Microscopy

Sample morphology of pine wood, carbonized porous template, activated templates and silicon carbide samples were observed using Hitachi S-3000N scanning Electron Microscope. SEM studies were carried out on shown in fig.2.13. The samples were mounted on the sample holder with the help of graphite tape. This tape act as both adhesive and as well as conducting material. Specimens were scanned at different magnifications. Silicon carbide samples being non conductive were coated with Pd-Pt metals in order to make conductive samples.

Figure 2.13 Scanning Electron Microscope (HITACHI-S3000N).
2.12.13 FT-IR Study:

Infrared spectra of the carbon and SiC fibers samples were recorded by using Shimadzu Infrared Spectrometer FT-IR 8000 shown in fig. 2.16

Samples were well grounded and made in to the powder form. After grinding, powder was mixed with dried KBr (Spectroscopic grade) powder and grinding again to make uniform mixture. Samples were prepared by pressing it in mold. The mold was fixed in FT-IR spectrometer sample holder & a spectrum was recorded. From the FT-IR spectrum various functional groups present in the samples were determined.

Figure 2.16 FT-IR Spectrophotometer (SHIMADZU FTIR-8000)
2.12.14 X-Ray Diffraction Analysis

XRD analysis of the carbonized template and silicon carbide was carried out by powder diffraction method using X-Ray Diffractometer Philips, X’pert model shown in Figure 2.17 having Cu Kα1 (λ-1.54056 Å) source. XRD gives information about the crystallinity of the SiC as well as crystalline and amorphous nature of samples. Wide angle (2θ = 10° to 80°) x-ray diffraction patterns were used to identify the material.
2.12.15 Raman Spectroscopy

Raman spectroscopy is a powerful and sensitive technique for studying the structure of amorphous and activated carbon. Raman spectroscopy was used to identify graphitic structure as well as crystallinity of prepared porous templates. The Raman spectra were taken with a Renishaw in via Raman microscope shown in Figure 2.18 using an argon ion laser at 514 nm excitation, using a 50× objective where the laser beam was focused in an area of ~1 μm.

Figure 2.18 Raman Microscope