

## Chapter 4

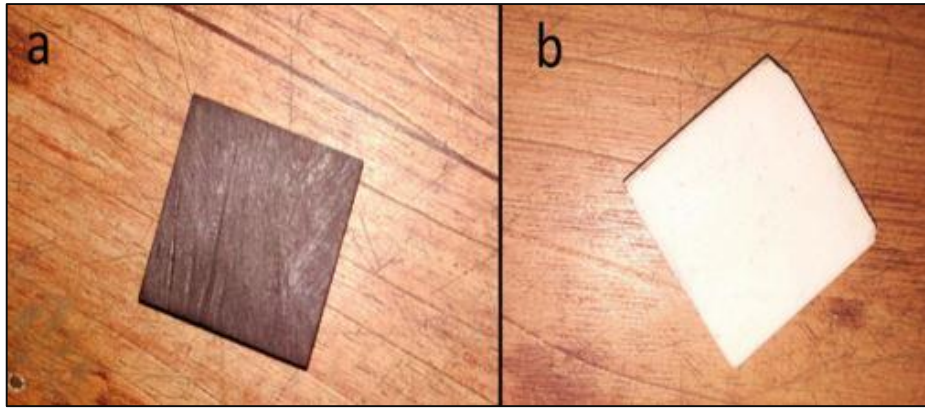
### Material Methodology and Experimental Procedure

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*Details of the experimental set-up, measurement of temperature at different locations, aerosol sampling and transport losses were discussed in the previous chapter. Before conducting an experiment, it is very important to prepare and characterize the sample to be tested as well as laying down procedures and experimental conditions. These details are presented in this chapter, which is divided into four sections. The physical dimension of the bare & alumina coated graphite sample and its properties are presented in the first section. In the second section, the elemental composition, structure and thermal behavior of the sample are analyzed using EDS, XRD and TGA techniques. The third section describes the experimental conditions and the procedure adopted for conducting the experiments. The last section describes the method for calculating the mass of graphite that gets converted into combustion products.*

#### 4.1 Material

A high-density isotropic graphite sample with 97.28% carbon content by weight was machined into pieces of size 25 mm x 25 mm x 5 mm having a weight approximately 7.0 g each (Figure 4.1a). Another sample of the same base dimensions was prepared by depositing a 100  $\mu\text{m}$  ( $\pm 10\%$ ) thick alumina coating on the graphite surface (Figure 4.1b). The plasma spray route was used to deposit the alumina coating onto the bare graphite. Two such pieces of the sample (either bare graphite or alumina coated graphite) were used in each experimental run. The salient physical properties of the bare graphite sample are shown in Table 4.



**Figure 4.1:** Picture of (a) bare graphite and (b) alumina coated graphite

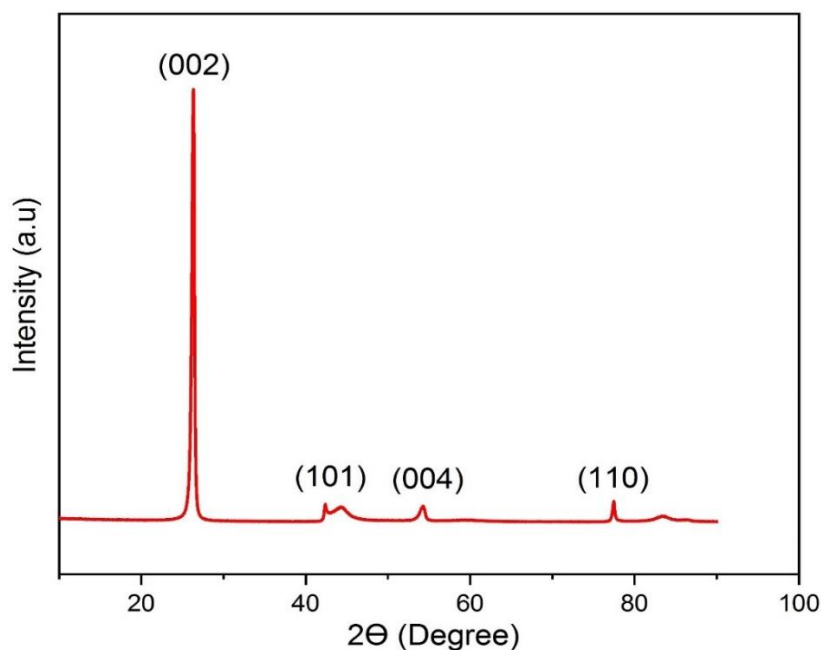
**Table 4.1:** Properties of graphite sample

<b>Properties</b>	<b>Value/details</b>
Mode of fabrication	Isostatically pressed
Particle size	2.5 micron
Density	1.82 g/cc
Porosity	10.57%
Pore size	4.6 micron
Compressive strength	113 MPa
Tensile strength	33 MPa
Flexural strength	40 MPa
Thermal conductivity	93 W/mK

## 4.2 Characterization of graphite sample

### 4.2.1 XRD analysis

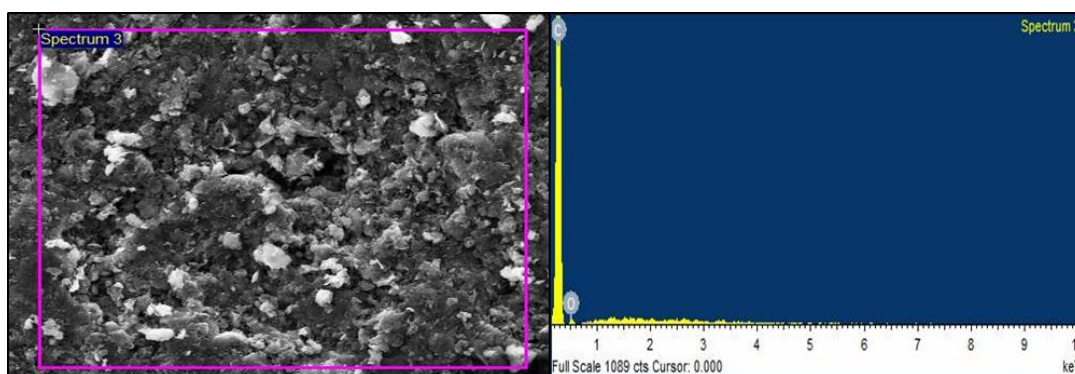
X-Ray Diffraction (XRD) is used to identify a material phase and it can provide data about lattice size. The XRD analysis of graphite samples was carried out using a Rigaku Miniflex 600 Desktop X-Ray Diffraction System (Rigaku Corporation, Japan), including a HyPix-400 MF 2D hybrid pixel array detector (HPAD) together with a 600 W X-ray source. The XRD pattern of the sample, shown in Figure 4.2, matched the standard graphite diffraction pattern (JCPDS card number: 08-0415). The major peaks correspond to the planes (002), (101), (004), and (110). The peak (002) was sharp in nature indicating the crystalline structure with an interlayer spacing of 0.346 nm.



**Figure 4.2:** XRD pattern of graphite sample

#### 4.2.2 EDS analysis

To examine the purity of bare graphite sample, the Energy Dispersive X-Ray Spectroscopy (EDS) analysis (Figure 4.3) was carried out and the elements present in the graphite sample were both qualitatively and quantitatively measured. The weight percentage of each element present in the spectrum was identified. It is observed from Figure 4.3 that graphite sample contains mostly Carbon (weight ~ 97.28%) and a small amount of Oxygen (weight ~ 2.72%).



**Figure 4.3:** EDS of graphite sample

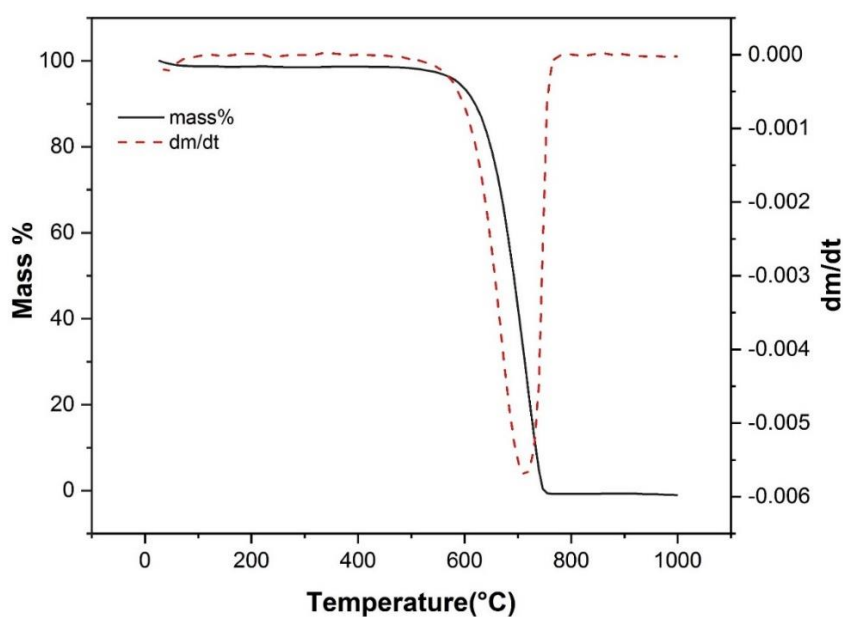
### 4.2.3 TGA analysis

Thermogravimetric analysis (TGA) was carried out to study the thermal behaviour of graphite in the temperature range of 30 - 1000 °C. Samples were run at 10 °C/min heating rate in an air environment as shown in Figure 4.4. It was observed that the thermal degradation temperature of graphite started around 600 °C, which means that graphite is stable up to about 600 °C in an air environment. Figure 4.4, also depicts that by heating up to 750 °C, around 99.5% weight was lost. The TGA results were also used to calculate the activation energy and order of reaction by using the Arrhenius equation (eq. 4.1). The activation energy and order of reaction were found to be 206 kJ/mol and 1 respectively.

$$\frac{dX}{dt} = A_e e^{-\left(\frac{E}{RT}\right)} X^n \quad 4.1$$

where non-dimensional mass

$$X = \frac{m - m_f}{m_o - m_f} \quad 4.2$$



**Figure 4.4:** TGA of graphite sample

## 4.3 Methodology

In this section, the detailed description of experimental methodology is described. Since the experiments were conducted under different conditions, this section is divided into two parts. The first section deals with the case when the samples were burnt at a constant temperature while the second is devoted to the case of burning carried out at different heating rates. The experimental condition and procedure for each case is also described in separate parts.

### 4.3.1 Experimental conditions

#### 4.3.1.1 Heating at constant temperature

The bare and alumina coated graphite samples were heated in an air stream within a closed chamber under various temperature conditions. The experiments were performed for five different test temperatures of 500, 600, 700, 800 and 900 °C at 25 Lmin<sup>-1</sup> air flow rate. The particle number concentrations in the exhaust were measured using a Nanoscan and an Optical Particle Sizer (OPS). Trace gases (CO and CO<sub>2</sub>) concentration were measured using a Gas analyser. In the present study, oxidation of graphite is done below 1000°C and hence oxide of Nitrogen are not measured. Oxides of Nitrogen are mostly formed at higher temperature in combustion with air above 1600°C. Molecular nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) in the combustion air dissociate into their atomic states and participate in a series of reactions.



In the OPS, negligible particles were observed compared to the Nanoscan, hence the results of only Nanoscan have been presented. While measuring the aerosol concentration, each experiment was repeated ten times to check for reproducibility.

During experiments, when the alumina tube was heated without inserting the graphite sample, some value of particle concentration was recorded by the spectrometers. We call this as the 'background particle concentration'. It is expected that some particles could be the leftover imprint from a previous experimental run. In the present work, the background particle concentration was found to be nearly constant and around  $10^3 \text{ \#/cm}^3$ .

#### **4.3.1.2 Heating at variable heating rates**

In the present work, the generation of graphite particles was predicted in the event of a hypothetical accident by air ingress in a nuclear reactor. Graphite heating was carried out at flow rates of 10, 15, 20, and 25  $\text{Lmin}^{-1}$  at four different heating rates of 2, 4, 6, and 8  $^\circ\text{C}/\text{min}$  (Figure 4.6). In the experimental unit, a single quartz tube was used instead of alumina and borosilicate tubes for the variable heating rate experiment. The reason is that the alumina tube cannot be used for heating rates above 4  $^\circ\text{C}/\text{min}$ . Nanoscan and Optical Particle Sizer were used to find the particle number concentration in the exhaust. A Gas Analyzer was used to measure trace gas levels (CO and CO<sub>2</sub>). Negligible particles were observed in the OPS as compared to the Nanoscan. Hence, in the present study, only the results of Nanoscan are presented.

#### **4.3.2 Experimental procedure**

At the start of each experiment, the furnace tube and boat were properly cleaned using a high-flow air jet. In a real situation the graphite moderator is expected to be exposed to the air ingress without obstructions offered by the surrounding geometry, we have tried to

replicate this in our experiment by placing the graphite samples in an alumina boat so that unobstructed air supply is made available.

Normal airflow was initiated using an air compressor unit and aerosol-measuring instruments monitored particle number concentration. If the number concentration was found to be more than  $10^3 \text{ \#/cm}^3$  (background particle concentration), the set-up was re-cleaned. Then the furnace was switched on and the heating was done according to the following two protocols:

**Heating protocol 1:** The procedure mentioned below was followed for analysis at different test temperatures of 500, 600, 700, 800, and 900 °C with different air flow rates of 10, 15, 20, and 25  $\text{Lmin}^{-1}$ .

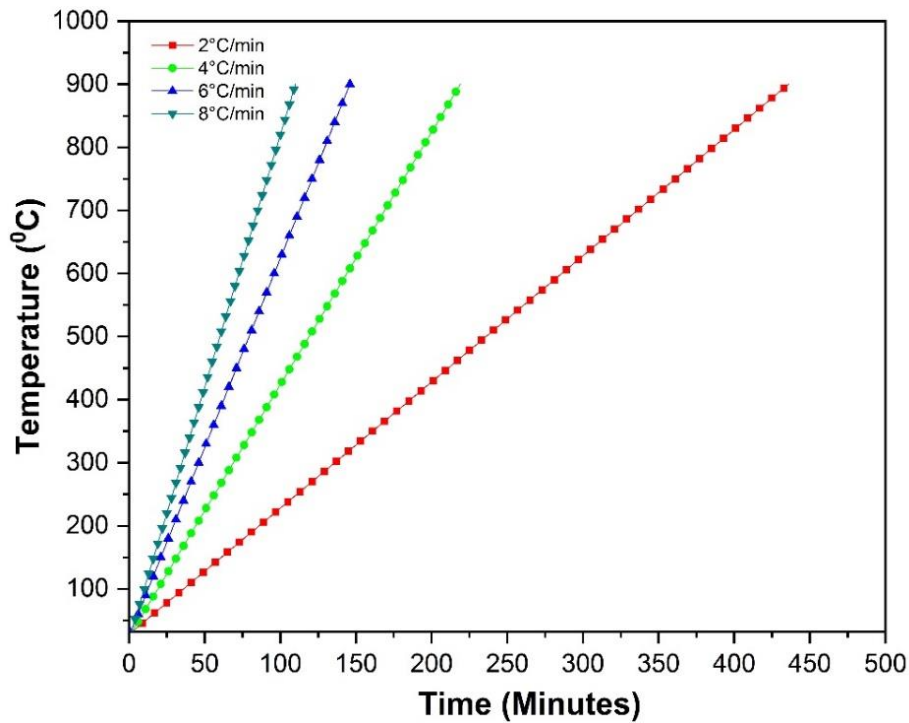
- The air flow was started at the desired flow rate.
- The furnace was heated up to 100 °C above the test temperature. This was done to ensure that any combustible material or residues of a previous experimental run get vaporized and purged from the set-up. The furnace was then cooled up to the required test temperature.
- The entrance of the alumina tube was opened and samples were placed in the boat. The boat was slipped back to the tube centre and the entrance was closed. The furnace temperature was kept constant for two hours at the test temperature and thereafter, the particle & gas concentration from the exit ports was measured.
- The furnace was allowed to cool to room temperature after the measurements. The residual sample in the boat was then removed for further analysis.

**Heating protocol 2:** Heating was carried out at flow rates of 10, 15, 20 and 25  $\text{Lmin}^{-1}$  at four different heating rates of 2, 4, 6 and 8 °C/min.

- Graphite sample was inserted in the quartz tube.
- The air flow was started at the desired flow rate.

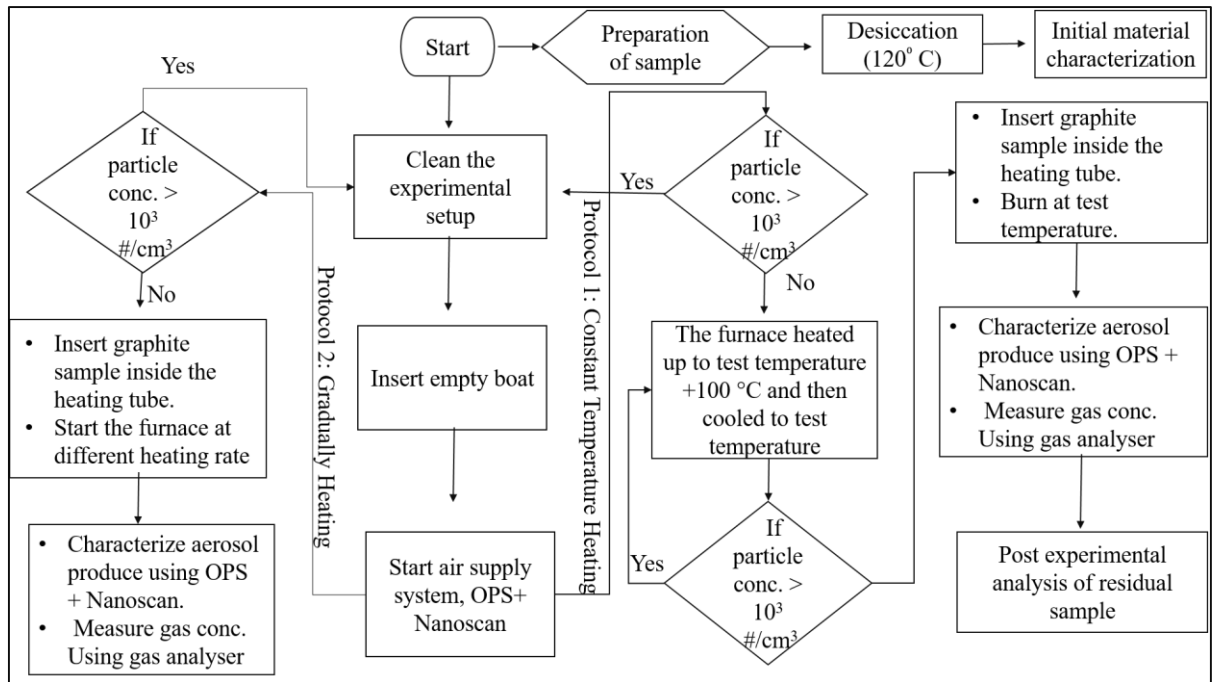
- The furnace was switched on, and allowed to heat the sample at different heating rates upto the maximum possible test temperature (900° C) (Figure 4.5).
- Readings from OPS, Nanoscan and Gas analyser were recorded.
- The furnace was allowed to cool to room temperature after the experiment. The residual samples were then removed for further analysis.

The various steps involved in the experiments have also been summarized below in the form of a block diagram (Figure 4.6).



**Figure 4.5:** Furnace heating rate





**Figure 4.6:** Block diagram of the experimental procedure

#### 4.4 Calculation of mass of graphite converted into combustion products

##### Mass of carbon converted into particles

- A plot of mass concentration versus time (data is taken from Nanoscan and OPS) is drawn and area under this curve is calculated.
- Assuming that the concentration in the heating tube is homogeneous, the calculated area is multiplied by the volumetric flow rate in the tube to obtain the mass of carbon that is converted into particles.

##### Mass of carbon converted into CO and CO<sub>2</sub>

- A plot of CO and CO<sub>2</sub> versus time (data is taken from Gas analyser) is drawn and by calculating the area under this curve, the total volume of CO and CO<sub>2</sub> generated is obtained.



From equation 4.3 and 4.4, we can see that number of moles of C converted into CO and CO<sub>2</sub> is same as number of moles of CO and CO<sub>2</sub> produced.

- Using the ideal gas equation,  $PV = nRT$ , the number of moles (n) of CO and CO<sub>2</sub> were calculated
- After multiplying n with 12, the molecular weight of carbon, the mass of carbon converted to CO and CO<sub>2</sub> was obtained.