CHAPTER THREE

3. Experimental

This section describes the experimental procedures, equipment, raw materials and chemicals used in this presented work. Where necessary, outlines of the equipment functions and how the analysis was conducted are given.

3.1 Raw Materials

The raw materials used were diamond powder, silicon powder, silicon wafers, phenolic resin powder, ammonium chloride powder, titanium powder. A fine grade of diamond (GR02 – average particle size of 1.5µm) was used. The particle size distribution of the diamond powder was analysed using a Malvern Mastersizer 2000 with water as the carrier fluid. (Fig. 3.1)

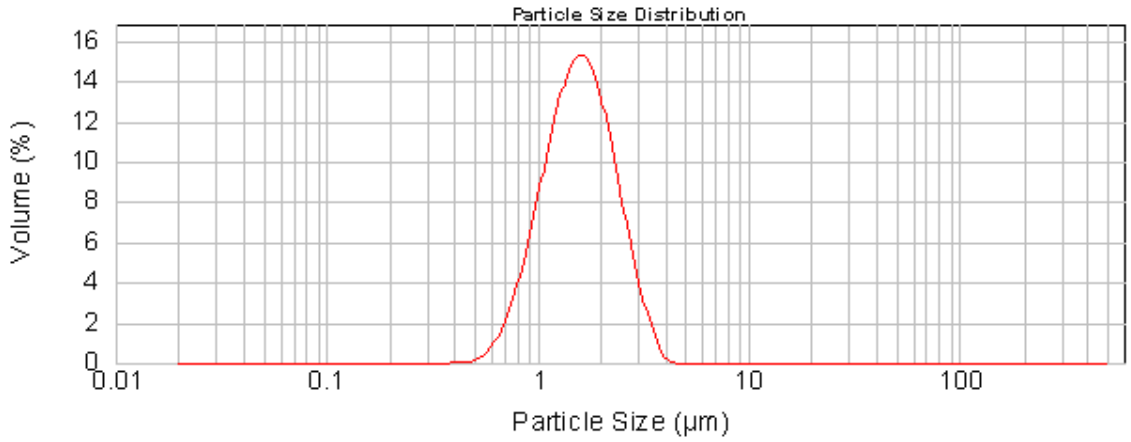


Fig. 3.1: *Particle size distribution of the fine-grained diamond powder.*

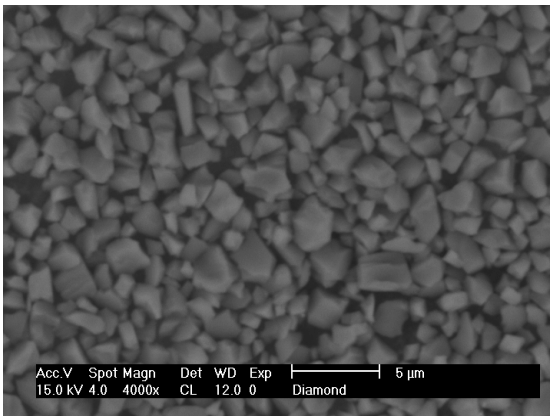
All the other materials used for the production and the synthesis of the SiC- diamond composites, their respective suppliers and purity are tabulated below: (Table 3.1)

Table 3.1: *Materials used and their respective suppliers.*

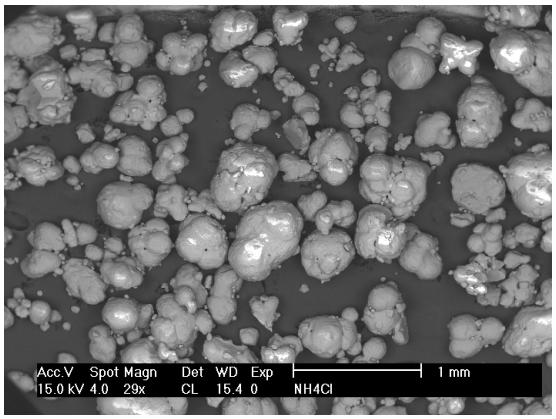
Material Name	Size	Supplier, Purity
Si powder	1-20 µm	Industrial Analytical, 99.9985%
Si wafer	1.7mm thick	Prolog Cemicol (Ukraine), 99.9999%
Phenolic resin powder	-	S.I. Group (South Africa), -
Ammonium chloride powder	-	Industrial Analytical, 99.5%
Ti powder	-60+100 mesh	Industrial Analytical, 99.5%
Acetone	-	Saarchem, 99.5%
Argon	-	Afrox, UHP 99.9%

3.1.1 Characterization of the powders

The morphology of the powders was characterized by a Scanning Electron Microscope (SEM).



a)



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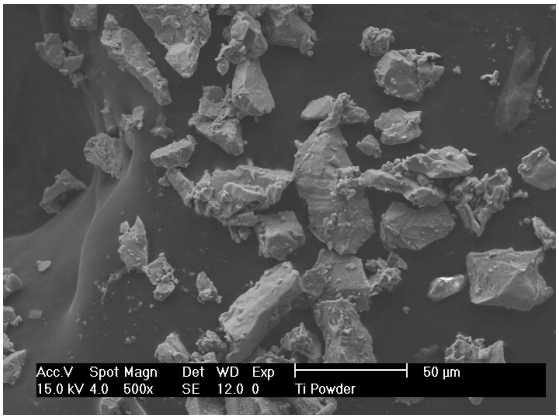
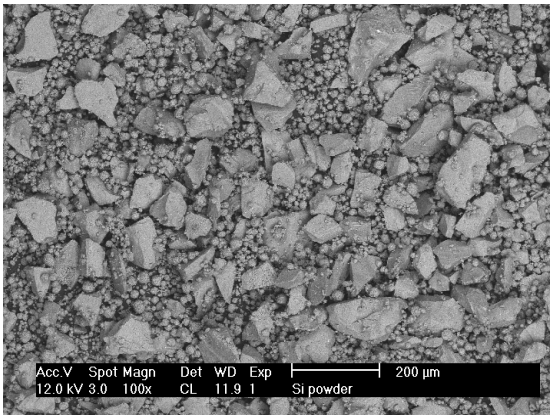


c)



d)

Fig 3.2: *SEM micrographs showing the morphology of the powders as received from the suppliers, namely* ***a)*** *diamond powder* ***b)*** *ammonium chloride powder* ***c)*** *titanium powder* ***d)*** *silicon powder*

3.2 Equipment Used

The following equipment was used in carrying out the experimental work.

3.2.1 The Tube Furnace

A horizontal type tube furnace (Elite TSH17/75/150), which operates to a maximum of 1 600^{0}C, was used for the coating of diamond with SiC and TiC experiments. It was also

used for the pyrolysis of the phenolic resin. The furnace consists of heating elements that are on the side walls and a platinum-rhodium thermocouple positioned in the heating chamber. A mullite tube, with a length of 1.2m and an inner diameter of 7.0cm, was used in the furnace. The tube is surrounded by a refractory board for insulation. The samples were placed in alumina boats and then put into the tube which was sealed on both ends to prevent the interference of the atmospheric gases. There is a temperature programme on the furnace for inputting the heating and cooling cycles. An argon atmosphere was used.

3.2.2 Uniaxial Hot Press

Infiltration experiments were carried out in a Hot Press (HP20 Thermal Technology). The Hot Press uses graphite heating elements for heating. The maximum attainable temperature is 2 100^0C and the maximum force that can be applied is 100KN. Water is used as the coolant for the furnace. The force is applied uniaxially by means of graphite punches. Vacuum in the chamber is maintained by use of a vacuum pump which can maintain a vacuum of 10mtorr. A gas flow is maintained in the chamber by means of a gas supply cylinder equipped with a suitable flow meter. The furnace also has a temperature programmer on the furnace for inputting the heating and cooling cycles.

All the graphite components that were supposed to be exposed to the sample zone were painted with an h-BN suspension that is stabilised by the use of poly-vinyl pyrrolidone. The suspension is made from mixing 37g of h-BN, 2g of poly-vinyl pyrrolidone and 100ml of water. The mixture is stirred vigorously using a magnetic stirrer. A paint brush is used to apply the mixture to the graphite pots, dies and punches.

3.2.3 X-Ray diffraction (XRD)

The phase composition of the elementary powders, the sintered powders and the sintered composites was determined by X-ray diffraction (Phillips PW1710 with a PW1830 diffractometer). A monochromatic Cu-Kα radiation at 40kV and 20mA was used over a 2θ angle from 20 to 80^0. A step scan time of 5 seconds was applied. Patterns were collected and phase identification was done using X'Pert HighScore software containing ICDD (International Centre for Diffraction Data) data files for comparison.

3.2.4 Particle size analyser

Particle size analysis and distributions (d_{10}, d_{50} and d_{90}) were determined by laser scattering in the wet cell section of a Malvern Mastersizer 2000 particle size analyzer. This instrument utilises Fraunhofer diffraction of light formed by particles with a diameter larger than the incident laser beam wavelength. The wet unit is equipped with ultrasonics to circulate the powder suspension through the sample cell. The Mastersizer 2000 was then used to capture the scattering pattern from the prepared samples. All measurements were done using the refractive index of the respective materials

3.2.5 Scanning electron microscope

A Phillips XL-30 SEM ESEM-FEG scanning electron microscope equipped with a field emission gun operating between 8-20kV was used to asses the microstructure of the polished samples. The samples were put on a carbon tape and mounted on the stage of the microscope. Secondary electrons were used to take images at a voltage of 10.0kV and a magnification range of 1000x-20000x at various spots. Element analysis was done using an energy dispersive spectrometer (EDS) analyser.

3.2.6 Image analyser

An image analyser was used for the analyses of polished samples and estimation of micro-cracks lengths used for fracture toughness measurements. The surfaces of samples were monitored to ensure complete removal of surface scratches at each grinding and polishing stage. The length of indentation crack formed during hardness testing was measured using AxioVision software. These were used to calculate the fracture toughness values of the high pressure sintered samples.

3.2.7 Hardness tester

A Vickers hardness tester was used for all the hardness measurements. This essentially consists of a diamond indenter in the form of a pyramid with a square base and an angle of 136^0 between opposite faces. A load of was applied to each sample and readings were taken from the scale provided on the machine. Conversion tables were used to obtain the Vickers' hardness numbers which were in turn converted to hardness values in GPa.

3.3 Preparation of the preforms

Green bodies were prepared for the infiltration trials. Three steps were employed in the preparation of these preforms, namely:

1. coating of the diamond powder
2. preparation of the preforms (compaction, curing and pyrolysing)

The infiltration experiments were conducted for three different types of preforms namely uncoated diamond, SiC coated diamond and TiC coated diamond.

3.3.1 Uncoated diamond

A pre-weighed amount of diamond powder (20g) was placed in a beaker and also a pre-weighed amount of phenolic resin was added to it. The resin content was varied at 5wt% and 10wt% of the total weight. The phenolic resin acted as a binder and a lubricant. To this mixture, 100ml of acetone was added per 100g of the mixture and the contents were stirred until all the resin dissolved.

The beaker, with the contents, was placed in a hot water bath (~90-100 ^{0}C) whilst being stirred continuously, to evaporate the acetone. As the emulsion became slurry-like, the temperature was reduced to about 50 ^{0}C to slow down the evaporation process. It was noted that when the acetone was evaporated off too fast, a hard cake was formed and could not be easily crushed into powder. When the slurry stiffened, the beaker was removed from the hot water bath. The agglomerated powder was crushed and screened through a -425 mesh sieve.

The screened powder (approx. 5g per tablet) was compacted into a green compact of 18mm diameter and 5mm height in a cold pressing steel die, for 5-10seconds. In order to vary the porosity of the preforms, the green bodies were compacted at different pressures. The pressures used were 45MPa, 35MPa, 25MPa, 20MPa and 10MPa. The green compacts were removed from the die and placed in an alumina boat in an oven at 120^{0}C for 15-18hrs in a curing chamber to cure the resin. The green compact was left to cool to room temperature and then weighed. After weighing, the preform was pyrolysed in a tube furnace, under an argon atmosphere. Pyrolysis destroys the phenolic resin leaving a carbonaceous coat on the diamond grains. Figure 3.3 shows the temperature cycle used.

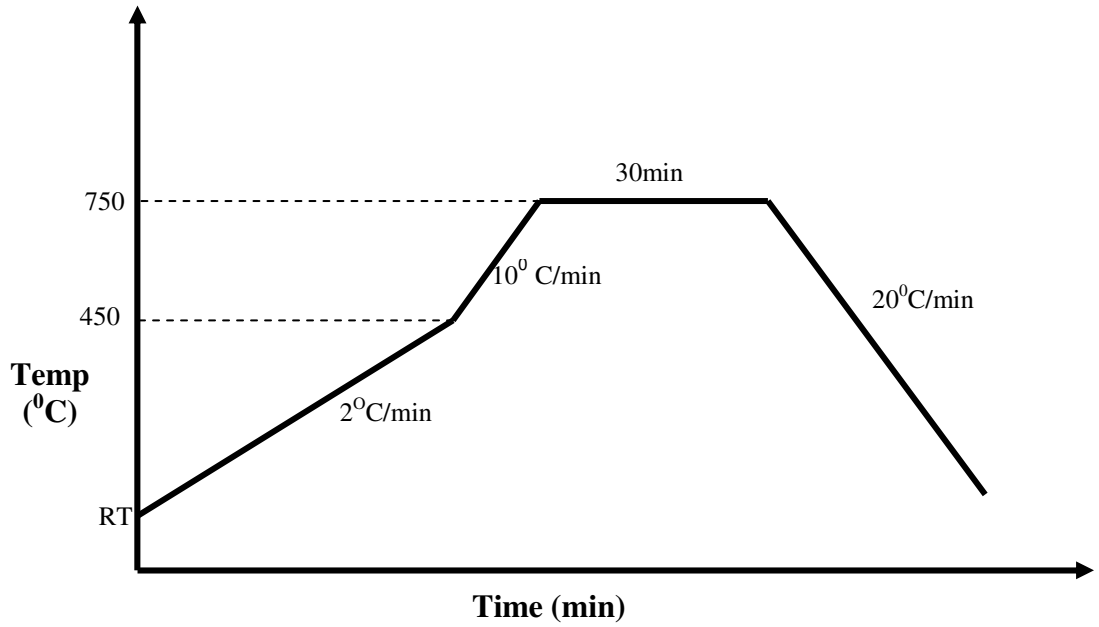


Fig 3.3: *The temperature-time cycle for the pyrolysis of the phenolic resin.*

After pyrolysis, the preform was weighed and then its dimensions were measured and recorded. This was done in order to calculate the green density and weight loss due to pyrolysis. Some pills are reserved for porosimetric measurements. Porosimetric measurements are done using a mercury porosimeter.

3.3.2 SiC coated diamond

The diamond powder (1.012g) was mixed with NH_4Cl (1.998g) and Si powder (1.055g) in an alumina boat. The powders were mixed in such a way that no diamond would be left unreacted (coated) and the reaction proceeded as follows:

$$NH_4Cl + Si + C \longrightarrow SiC + NH_3 + HCl \qquad (3.1)$$

From the above reaction, silicon tetrachloride is formed first, which 'reacts' with C (diamond), thus transporting the Si to the diamond surface forming a SiC coating on the diamond particles. These quantities were calculated as part of an effort to achieve a coating of 1µm thickness on the surface of the diamond particles. The mixture was heated in an argon atmosphere (at a flow rate 5L/min) in a tube furnace. The temperature was ramped up at 10^0C/min up to 1300^0C and kept there for 1hour. Cooling to room temperature took place at 5^0C/minute. The sequence is illustrated schematically below (Fig. 3.4).

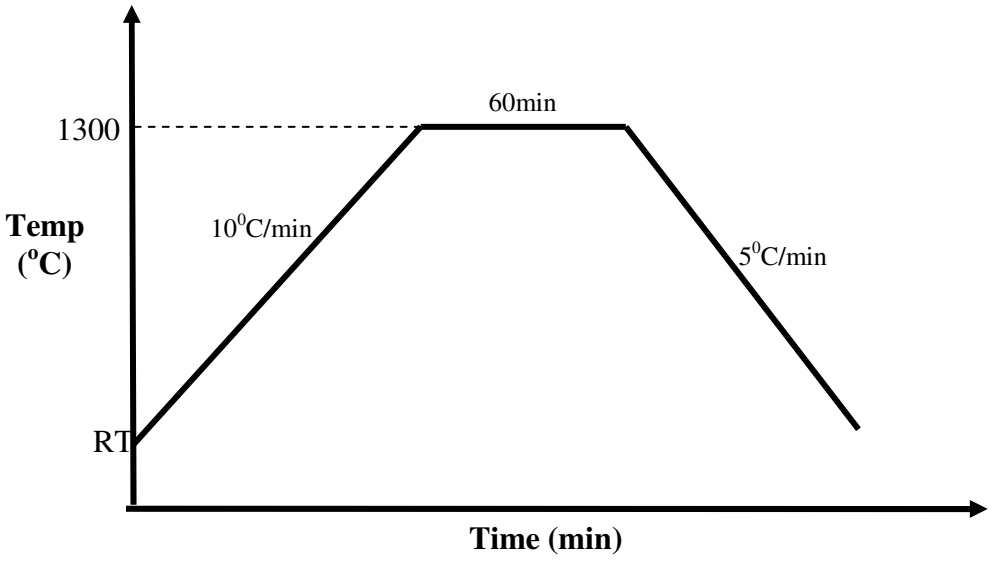


Fig 3.4: *The temperature-time cycle for coating of diamond powder with SiC.*

The resulting powder was analysed using the SEM and the XRD. The preforms for infiltration were produced in the same way as for the uncoated diamond powder. The green densities and porosity were also measured in the same manner.

3.3.3 TiC coated diamond

The diamond powder (1.030g) was mixed with NH_4Cl (2.078g) and Ti powder (1.882g) in an alumina boat. The powders were mixed in such a way that no diamond would be left unreacted (coated) and the reaction proceeded as follows:

$$NH_4Cl + Ti + C \longrightarrow TiC + NH_3 + HCl \qquad (3.2)$$

From the above reaction, titanium tetrachloride is formed first, and it 'reacts' with C (diamond), thus transporting the Ti to the diamond forming a TiC coating on the diamond particles. These quantities were calculated trying to achieve a coating of 1μm thickness on the diamond particles. The mixture was heated in an argon atmosphere (at a flow rate 5L/min) in a Tube furnace. The temperature was raised at 5^0C/min up to 750^0C and soaked for 1hour. Cooling to room temperature occurred at 5^0C/minute (Fig 3.4). The resulting powder was analysed using the SEM and the XRD.

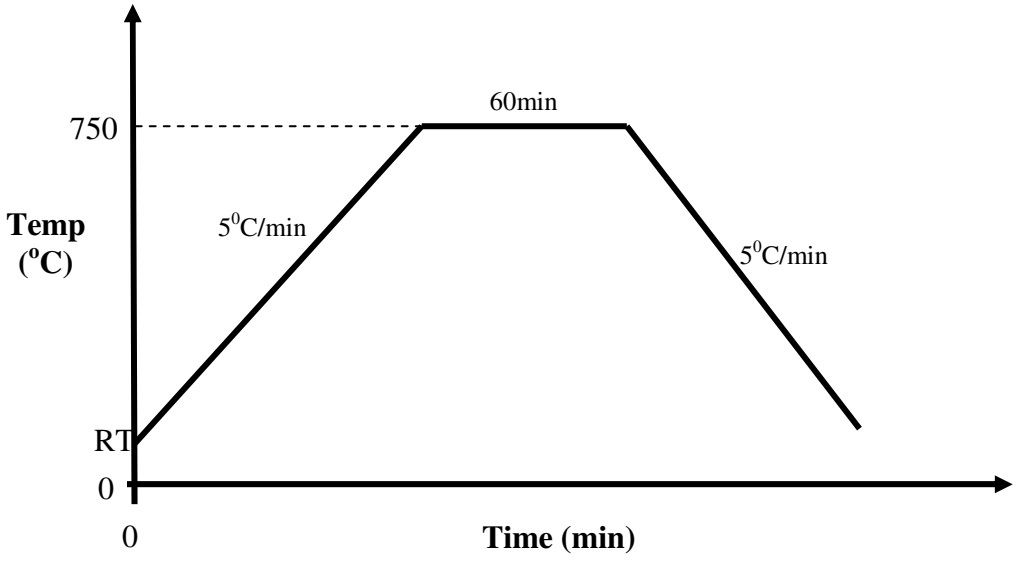


Fig 3.5: *The temperature-time cycle for coating of diamond powder with TiC.*

The preforms for infiltration were produced in the same way as for the uncoated diamond powder. The green density and porosity were also measured in the same manner as for the uncoated diamond.

3.4 Infiltration of the preforms

Infiltration experiments were done in the Uniaxial Hot Press. The principle is illustrated in Figure 3.6 below. The preforms were infiltrated with silicon in a graphite pot. An argon atmosphere was used throughout the sintering cycle. The silicon wafer was cut to tablets of 18mm in diameter. The graphite pot and the lid were first coated with an h-BN suspension and the suspension was left to dry. The silicon tablet was put at the bottom in the graphite pot. The preform was then placed on top of the silicon wafer and the whole set-up was covered with an h-BN coated graphite lid and put in a hot press for infiltration. Small silicon carbide spacers (2mm x 2mm x 3mm) were put between the silicon wafer and the preform to separate these two tablets so that no reaction takes in the solid state during heating up.

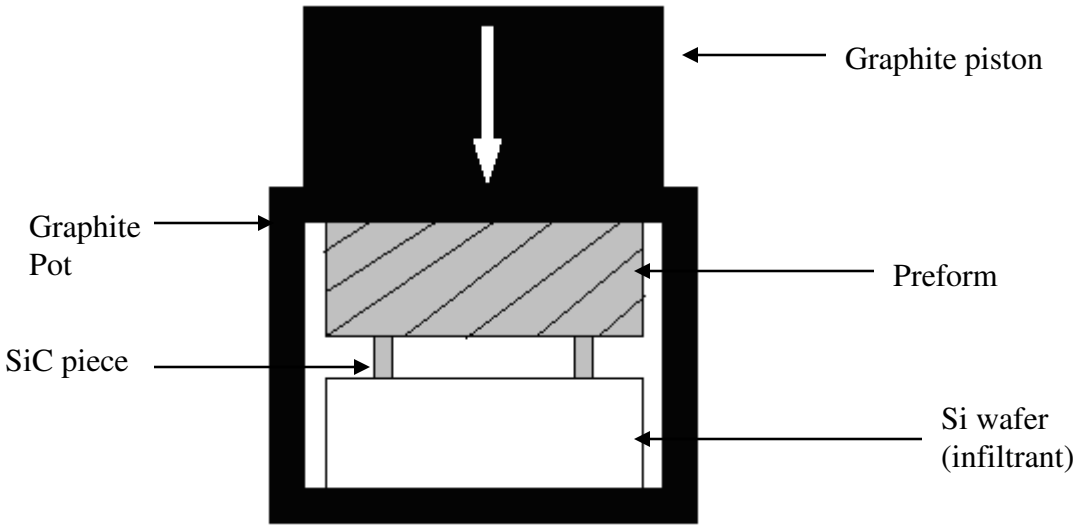


Fig 3.6: *The set-up of the preform and the silicon wafer before infiltration.*

This set up was heated in the Uniaxial Hot Press using the temperature-pressure-time cycle illustrated in Fig 3.7 below. A pressure of 20MPa (added gradually) was applied onto the sample through the piston when the temperature reached +/- 1400^0C (softening temperature of Si) to bring the melt and the preform into contact hence infiltration could start. The pressure was removed when the temperature reached 1400^0C on cooling down.

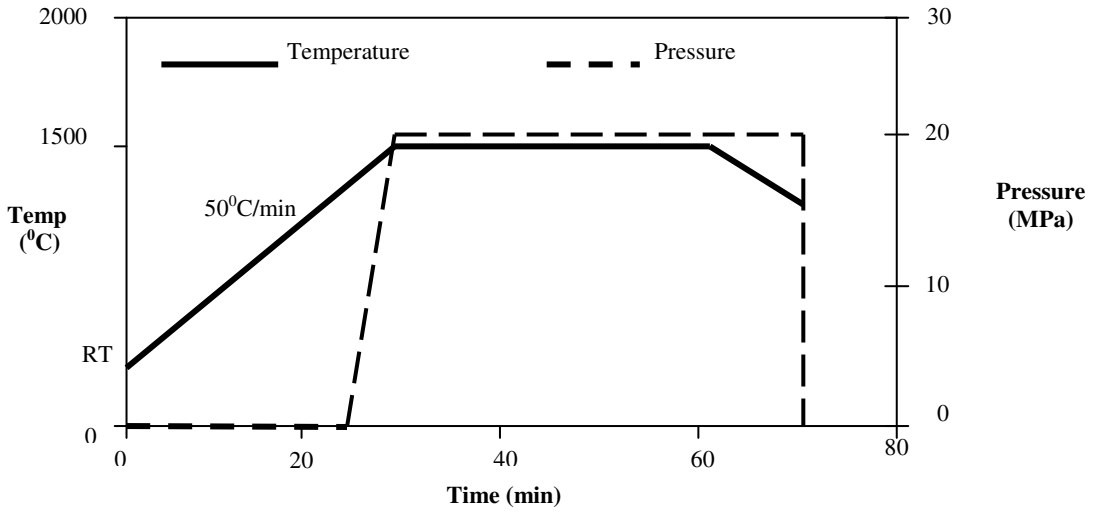


Fig 3.7: *The temperature-pressure-time cycle for infiltration of the preforms with silicon.*

When the furnace had cooled, the graphite pot was removed from the furnace and was broken to retrieve the infiltrated product. The infiltrated product was cross-sectioned using a laser. The cross-sections were polished using resin bonded diamond wheels with 1µm diamond at 300rpm prior to characterisation with SEM and XRD. The phase composition of the infiltrated material was determined by quantitative analysis using the Image Tool 3.

3.5 Analysis of the products

The infiltrated samples were cross-sectioned into two halves using a laser. One half was polished and then analysed using the Scanning Electron Microscope, X-Ray Diffractometer and the Image Tool. The Image Tool was used to determine the amount of phases present in the composites made. The other half was used for density/porosity determination. Both halves were later on used for wear behaviour analysis.

3.5.1 Polishing of the Samples

The cross-section of the sample to be polished was first lapped for 30 minutes on a standard lapping wheel using 350μm diamond grit. Samples were then further lapped with a finer grit (120μm) for 20 minutes. This was done in order to remove the scratches on the surface of the samples from the 350μm diamond grit lapping. After lapping, the samples were polished using a 1μm resin bound diamond wheel with an outside diameter of 200mm and a blade width of 25mm at 300 rpm. A force of 400N was applied during the polishing and the polishing continued until a mirror finish was obtained.

3.5.2 Density Measurements

The sintered density was determined by the standard Archimedes' method which consisted of the following steps;

i.) The dry weight of the sample *(m_d)* was determined using a balance. (Used for all the weight measurements).

ii.) Sample was boiled in distilled water for 3hours.

iii.) The suspended weight of the sample *(m_s)* was determined.

iv.) The surface moisture was removed by a light wipe with a paper towel to remove excess water from the surface and the wet weight *(m_w)* determined.

v.) The procedure (steps (i) to (iv)) was repeated to check consistency in weighing.

The open porosity (P_o) and density (ρ_s) were determined using the following equations:

$$\rho_s = \frac{m_d \rho_{water}}{(m_s - m_w)} \tag{3.3}$$

$$P_0 = \frac{m_w - m_d}{m_w - m_s} x100\% \tag{3.4}$$

Where, m_s = suspended mass

m_w = water saturated mass

m_d = dry mass

P_o = open porosity

3.5.3 Phase composition (Image Analysis)

The phase composition of the composites made was done using the image tool 3. Using image analysis software program (AnalySIS "Pro"), the percentage of the each phase present in the composites were determined. The method used to determine the percentage of the phases was by measuring the area of light intensity of the different phases. Mostly three phases were present namely, diamond phase (darker), SiC phase (grey) and sometimes Si phase (white).

3.5.4 Wear Testing Measurements

For wear testing measurements, the infiltrated sample was cut into 5 x 5 mm dimensions and making a 30^0 rake angle on the cut pieces. The cut sample pieces were then mounted onto the tool holder on a lathe which had a rotating cylinder of resin-bonded silica flour for work piece. The work piece was machined off the cylinder with the composite piece

for a set time (Fig 3.8). The piece was taken off and the wear scar measured using an optical microscope with suitable software for sample dimensional measurement. This was repeated on the same work piece for several times in order to generate a plot of wear scar against machining time. The work piece was further analysed using SEM to determine the nature of wear.

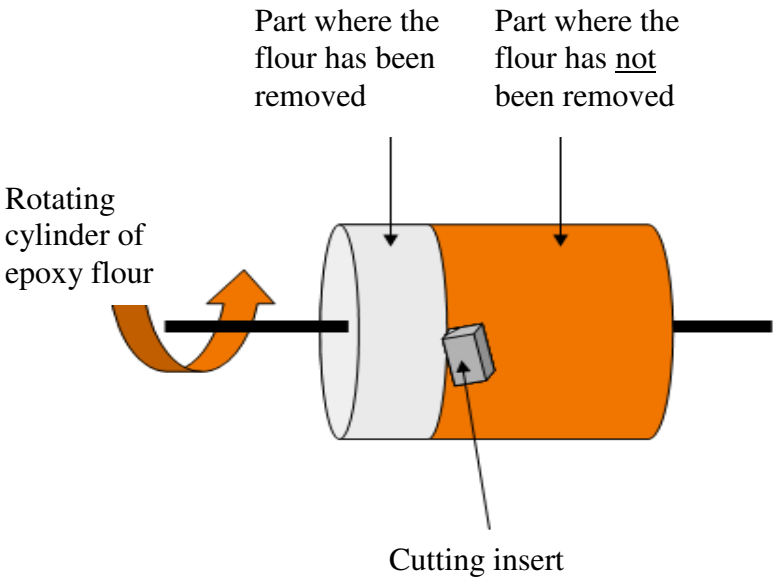


Fig. 3.8: *Wear test using a rotating cylinder of resin-bound epoxy flour conducted on the infiltrated material produced.*