CHAPTER FOUR

4. Experimental Results

This section presents the results obtained from the coating experiments of diamond powder with SiC and TiC, the infiltration results of the preforms made from the coated and uncoated diamond powders, characterization of the materials made using XRD, SEM and optical microscope. Different temperature cycles were explored in order to optimize the coating conditions. Mechanical properties (wear behaviour and hardness) of the composites made were also determined.

4.1 Coating of diamond

4.1.1 SiC coating

The diamond powder was premixed with NH₄Cl and Si as described in section 3.3.2. Different heating profiles were initially employed in order to optimize the coating conditions. The holding temperatures were varied at 1250°C, 1300°C and 1350°C and were done in an argon atmosphere. The chemical compositions, microstructure and surface morphology of the coatings were analysed using the SEM and XRD.
Fig 4.1: SiC coating of diamond powder at a holding temperature of 1250°C a) SEM micrograph b) XRD pattern and c) Peak matching list, of the powder
Fig 4.2: SiC coating of diamond powder at a holding temperature of 1300°C a) SEM micrograph b) XRD pattern and c) Peak matching list, of the powder
Chapter 4: Results

Fig 4.3: SiC coating of diamond powder at a holding temperature of 1350°C a) SEM micrograph b) XRD pattern and c) Peak matching list, of the powder
X-Ray diffraction patterns and SEM micrographs were obtained on the SiC coatings on diamond at different soaking temperatures to determine the morphology and phases present in the coatings. The XRD pattern showed that coating of diamond with SiC occurred though the coating is more significant at 1300°C. This is explained by the peak intensities of SiC at 1300°C. At 1350°C, there was some unreacted elementary Si in the product. For the preparation of the infiltration preforms, the diamond was coated with Si at a holding temperature of 1300°C because that is when the best coating was achieved and no other phases were present except SiC and diamond.

### 4.1.2 TiC coating

The diamond powder was premixed with NH₄Cl and Ti as described in section 3.3.3. Different heating profiles were initially employed in order to optimize the coating conditions. The chemical compositions, microstructure and surface morphology of the coatings were analysed using the SEM and XRD.
Fig 4.4: TiC coating of diamond powder at a holding temperature of 600°C a) SEM micrograph b) XRD pattern and c) Peak match list, of the powder
Fig 4.5: TiC coating of diamond powder at a holding temperature of 700°C a) SEM micrograph b) XRD pattern and c) Peak match list, of the powder
Fig 4.6: TiC coating of diamond powder at a holding temperature of 800°C a) SEM micrograph b) XRD pattern and c) Peak match list, of the powder

X-Ray diffraction patterns and SEM micrographs were obtained on the TiC coatings on diamond at different soaking temperatures to determine the morphology and phases present in the coatings. The XRD pattern showed that coating of diamond with TiC
occurred at all temperatures tried, but the coating is more suitable in terms of composition at 700°C. At 700°C only diamond and TiC were formed. At 600°C, TiC$_{0.3}$N$_{0.7}$ was formed. TiN and TiC were formed at 800°C. For the preparation of the infiltration preforms, the diamond was coated with Ti at a holding temperature of 700 °C because that is when the best coating with TiC was achieved and no other phases were present except TiC and diamond.

4.2 Diamond-silicon carbide composites produced by infiltration of uncoated diamond with Si.

4.2.1 Preform Structure

After the preparation of the preforms, they were pyrolysed in an argon atmosphere to burn off the resin. After pyrolysis, the preforms’ green density was determined using the mass and volume of the preform and the pore size distribution was determined using the mercury porosimeter after pyrolysis. At 5wt% resin, the lowest compaction pressure was 25MPa because below that, the preforms were very friable. These results are presented below.
Fig 4.7: Relationship between pressure and porosity at different resin content after pyrolysis at 750°C for 30 minutes.

Fig 4.8: Relationship between pressure and pore size at different resin content after pyrolysis at 750°C for 30 minutes.
Chapter 4: Results

A study on the sintering of fine-grained diamond-SiC composites

Fig 4.9: Relationship between pressure and green density at different resin content after pyrolysis at 750°C for 30 minutes.

Fig 4.10: The pore size distribution of preforms with varying compaction pressure at 10wt% resin content after pyrolysis at 750°C for 30 minutes.
From the graphs above (Figs. 4.7, 4.8 and 4.9), it can be noted that as the resin content increases, there is a general decrease in the green density, the open porosity and nearly no change of the pore size. As the phenolic resin is less dense than the diamond, an increase in the resin content causes a decrease in the theoretical density of the preforms. The reduction of the green density with increasing resin content is less than the reduction of the theoretical density. This can be attributed to the fact that, as the resin acts as a lubricant and in its presence the powder therefore compacts more easily. Thus when using the same compaction pressure, the high resin content powder would compact into a less porous green body than a low resin one.

When the compaction pressure effect is taken into account, it can be seen that an increase in the compaction pressure causes a decrease in the overall porosity and an increase in the green density though the pore size of the preforms remain constant, regardless of the resin content. The porosity decreases because at higher compaction pressures, the preforms will be more compact than at low pressures hence closing down the pores.

4.2.2. Infiltration of uncoated diamond preforms

Grade 2 (1.5µm) uncoated diamond was infiltrated with silicon. A phenolic resin binder was used and its content was set at 5wt% and 10wt% during the making of the preforms. Also the green compaction pressure was varied at these resin contents. Micrographs in figures 4.11 and 4.12 show the infiltration depths in the samples. Only the maximum infiltration heights are shown.
**Fig. 4.11:** Cross-section showing the maximum infiltration height after infiltration at 1500 °C for 30 minutes of grade 2 diamond with 10wt% resin at 20MPa.

**Fig. 4.12:** Cross-section showing the maximum infiltration height after infiltration at 1500 °C for 30 minutes of grade 2 diamond with 10wt% resin at 25MPa.
Several infiltration experiments were carried out on uncoated diamond. These infiltration results are summarized in Table 4.1. The infiltration product is fully dense because no pores were evident under the SEM. It seems that increasing the resin content helped improve the infiltration depth attained. Also, an increase in open porosity of the green body (low compaction pressure), gave rise to an increase in the infiltration depths as well. There was some agglomeration that could be seen on the micrographs (Fig 4.11 and 4.12) because two distinct spots could be seen where some areas were a bit darker than the other areas. The agglomeration of the diamond particles observed is suspected to be due to the inhomogeneity in the green compact, caused by the method utilized to break the agglomerates after the introduction of the phenolic resin and subsequent drying. The micrographs of the infiltrated material are shown in Figures 4.13 and 4.14 below.

**Fig. 4.13:** Micrograph from resin-bonded (10 wt% resin) grade 2 diamond infiltrated with silicon at 10MPa (overall vol% composition (Image Tool): Diamond = 37; SiC = 63 and Si = 0)
An inhomogeneous distribution of the diamond (dark phase) within the silicon carbide matrix (grey phase) is observed in Fig 4.14. This can be attributed to the agglomerates formed as described earlier on Page 61 (Fig 4.11 and 4.12). Since the particle size of the diamond used is smaller, the reaction to form SiC seems to consume free silicon completely. This is due to a combination of the large surface area that promotes fast reaction and the small pores with little silicon and thin SiC layer formed through which silicon and carbon migrate short distances to react. The grey phase in Fig. 4.14 is SiC, no free Si phase was detected and the white phase seen is contamination from polishing.
Table 4.1: A summary of the infiltration results for uncoated diamond preforms (Temp = 1500°C and time = 30mins)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Green Compaction Pressure (MPa)</th>
<th>Weight Loss (%) (after pyrolysis)</th>
<th>Green Density (g/cm³) (after pyrolysis)</th>
<th>Mean Pore Diameter (µm)</th>
<th>Open Porosity (%)</th>
<th>Base</th>
<th>Sides</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR02PR05</td>
<td>25</td>
<td>1.82 ± 0.04</td>
<td>1.78 ± 0.01</td>
<td>0.58 ± 0.01</td>
<td>46 ± 0.7</td>
<td>2.82 ± 0.06</td>
<td>2.96 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1.93 ± 0.02</td>
<td>1.79 ± 0.01</td>
<td>0.59 ± 0.01</td>
<td>45 ± 1.4</td>
<td>2.78 ± 0.04</td>
<td>2.90 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>1.86 ± 0.07</td>
<td>1.81 ± 0.01</td>
<td>0.59 ± 0.01</td>
<td>43 ± 1.4</td>
<td>2.70 ± 0.06</td>
<td>2.66 ± 0.10</td>
</tr>
<tr>
<td>GR02PR10</td>
<td>10</td>
<td>3.94 ± 0.06</td>
<td>1.71 ± 0.01</td>
<td>0.55 ± 0.01</td>
<td>41 ± 1.4</td>
<td>3.31 ± 0.03</td>
<td>3.30 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.86 ± 0.01</td>
<td>1.74 ± 0.02</td>
<td>0.57 ± 0.01</td>
<td>38 ± 0.7</td>
<td>3.09 ± 0.05</td>
<td>3.06 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3.89 ± 0.07</td>
<td>1.75 ± 0.01</td>
<td>0.56 ± 0.01</td>
<td>36 ± 1.4</td>
<td>2.97 ± 0.03</td>
<td>2.94 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.05 ± 0.03</td>
<td>1.76 ± 0.01</td>
<td>0.57 ± 0.01</td>
<td>35 ± 0.7</td>
<td>2.90 ± 0.03</td>
<td>2.80 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>4.02 ± 0.01</td>
<td>1.77 ± 0.01</td>
<td>0.57 ± 0.01</td>
<td>34 ± 1.4</td>
<td>2.90 ± 0.07</td>
<td>2.58 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.98 ± 0.04</td>
<td>1.79 ± 0.02</td>
<td>0.56 ± 0.01</td>
<td>31 ± 0.7</td>
<td>2.70 ± 0.06</td>
<td>2.54 ± 0.01</td>
</tr>
</tbody>
</table>

Legend:
GR02PR05 = Grade 2 diamond with 5wt% phenolic resin content.
GR02PR10 = Grade 2 diamond with 10wt% phenolic resin content.
NB: All experiments with uncoated diamond were carried out in an Ar environment.
4.2.3 Mechanical and wear properties of the produced composite.

4.2.3.1 Wear Behaviour Tests

In order to get an indication on the wear behaviour of the composites produced, epoxy resin-bonded silica flour was used to abrade the composites made in a machining experiment. For this work, composites produced at a green compaction pressure of 25MPa and 10wt% resin was used. The depth of the cut and the feed rate used were 1mm and 0.3mm/rev respectively. The abrading tests were carried out at cutting speeds of 100m/min and 400m/min. The scars produced on the sample during abrading with epoxy resin were measures and plotted against time. These were compared to wear behaviour of the syndax material and composites produced by K. Mlungwane \cite{27} in her PhD work. For hardness determination, the indentation method with a diamond indenter was employed at room temperature. The wear behaviour data is presented in figures 4.15 and 4.16.

![Wear Test at 100m/min](image)

**Fig 4.15:** A comparison of the wear behaviour of the composite material made against that of Element Six Syndax material and the composite material produce by K. Mlungwane \cite{27}, at a cutting speed of 100m/min.
Fig 4.16: A comparison of the wear behaviour of the composite material made against that of Element Six Syndax material and the composite material produce by K. Mlungwane\textsuperscript{[27]}, at a cutting speed of 400m/min.

Syndax is a commercially available diamond-silicon carbide composite that is mainly used in wear application in the oil and gas industry. Syndax is produced under high pressure/high temperature conditions and has more than 90 vol\% diamond thus much less binder phase than the composite produced in this work. Syndax is made from a multi-grained diamond powder and has an average diamond grain size of 20\(\mu\)m whereas the material made in this work is made from a single grain size distribution of diamond of particle size 1.5\(\mu\)m.
Fig 4.17: A comparison SEM micrograph of a) Syndax and b) the material made in this work (25MPa, 10wt% resin), showing the higher diamond/lesser binder content in Syndax than in the composite and also some diamond-diamond contact in the former.
The composite material that was produced performed slightly better at a lower cutting speed of 100m/min than at a higher cutting speed of 400m/min. Though in both instances Syndax outperforms the diamond-silicon carbide composite made in this work but their performance is comparable. The composite made from this work and syndax far outperforms the composite made from grade 22 (17µm) diamond by K. Mlungwane[^27] in her PhD work, at both cutting speeds.

The wear scars of both syndax and this composite material made were analyzed using the scanning electron microscope after machining for 50seconds at a cutting speed of 400m/min. The results are given in Figure 4.18 below.
**Fig. 4.18**: SEM micrographs of the wear scars of **a)** the composite material made (25MPa and 10wt% resin) and **b)** Syndax, after wear at 50 seconds.
From Fig. 4.18 above, it can be seen that the wear scar surface has some grooves and protrusions. The protrusions are diamond particles and the grooves are a result of the erosion of SiC, the softer phase.

4.2.3.2 Hardness Tests

Hardness measurements were carried out using the indentation method. Only material made at 25MPa with 10wt% resin was indented. No more further indentation was carried out on other material because the indenter broke. The indented material is shown in the micrograph in Fig 4.19 below.

![SEM micrograph showing the indent on the composite made.](image-url)
The indents on the composite are not well defined and formed due to the breaking of the diamond indenter. The load was increased gradually from 5kg to 35kg, but before the 35kg load, no indent could be formed. From the indent formed, it was very difficult to calculate the fracture toughness of the composite because measuring the diagonals of the indent would be highly erroneous and would not represent the true value. Also measuring the fracture length values would carry a large error. Therefore such measurements would not represent the true value of the fracture toughness of the composite. The propagation of the cracks on the composite from the indent is shown in Fig. 4.20 below.

Fig. 4.20: SEM micrographs showing the propagation of cracks from the indent produced on the composite made.

From analysis of the nature of the fracture, there was evidence of some trans-granular cracking. It can therefore be concluded that the diamond is strongly bound to the SiC matrix.
4.3 Diamond-silicon carbide composites produced by infiltration of SiC-coated diamond with Si.

4.3.1 Preform Structure

After the preparation of the preforms, the preforms’ green density was determined using the mass and volume of the preform. At 5wt% resin, the lowest compaction pressure was 25MPa because below that, the preforms were very friable. These results are presented below. The porosity and the pore size distribution could not be measured because the porosimeter was out of order.

**Fig. 4.21:** Relationship between pressure and green density at different resin content for SiC coated diamond.
From the graph, Fig. 4.21, it can be seen that as the resin content increases, there is a general decrease in the green density. It can be inferred from the results of uncoated diamond preforms, that there will be a general decrease in porosity with an increase in resin content. The reasons for this have been explained earlier in the making of uncoated diamond preforms.

When the compaction pressure effect is taken into account, it can be seen that an increase in the green compaction pressure causes a decrease in the overall porosity and increases in the green density and pore size of the preforms regardless of the resin content. The porosity decreases because at higher compaction pressures, the preforms will be more compact than at low pressures hence closing down the pores.

### 4.3.2. Infiltration of SiC-coated diamond preforms

SiC-coated diamond (Grade 2 (1.5µm)) was infiltrated with silicon. Problems were encountered during the infiltration of SiC-coated diamond. At first, infiltration could not take place at all. The silicon would just solidify and attach itself to the preform. It was suspected that a layer of SiO$_2$ was formed on the base of the preform thus reducing its wettability (of the diamond particles by silicon) and preventing the onset of infiltration. In order to curb this problem, the preforms to be infiltrated were heated at 1300°C for one hour, in an argon atmosphere, to ‘evaporate’ the SiO$_2$ before infiltration. Infiltration of preforms with 10wt% phenolic resin was also tried in vacuum. Table 4.2 shows a summary of the infiltration results of SiC-coated diamond preforms.
Table 4.2: A summary of the infiltration results for SiC-coated diamond preforms
(Temperature = 1500°C and time = 30min).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Green Compaction Pressure (MPa)</th>
<th>Weight Loss (%) (after pyrolysis)</th>
<th>Green Density (g/cm³) (after pyrolysis)</th>
<th>Max. Infiltration Depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Base</td>
<td>Sides</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.64 ± 0.08</td>
<td>1.93 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>1.98 ± 0.04</td>
<td>1.91 ± 0.02</td>
<td>2.22 ± 0.06</td>
<td>2.18 ± 0.03</td>
</tr>
<tr>
<td>GR02PR05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>1.59 ± 0.04</td>
<td>1.89 ± 0.01</td>
<td>2.48 ± 0.05</td>
<td>2.48 ± 0.11</td>
</tr>
<tr>
<td>25</td>
<td>1.84 ± 0.01</td>
<td>1.86 ± 0.01</td>
<td>2.52 ± 0.11</td>
<td>2.50 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>3.68 ± 0.07</td>
<td>1.89 ± 0.01</td>
<td>2.54 ± 0.08</td>
<td>2.48 ± 0.11</td>
</tr>
<tr>
<td>45</td>
<td>3.66 ± 0.01</td>
<td>1.88 ± 0.01</td>
<td>2.72 ± 0.01</td>
<td>2.60 ± 0.08</td>
</tr>
<tr>
<td>35</td>
<td>3.74 ± 0.04</td>
<td>1.87 ± 0.01</td>
<td>3.05 ± 0.06</td>
<td>3.00 ± 0.01</td>
</tr>
<tr>
<td>GR02PR10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>3.88 ± 0.01</td>
<td>1.84 ± 0.02</td>
<td>3.44 ± 0.08</td>
<td>3.19 ± 0.06</td>
</tr>
<tr>
<td>20</td>
<td>4.02 ± 0.07</td>
<td>1.83 ± 0.02</td>
<td>3.51 ± 0.07</td>
<td>3.42 ± 0.05</td>
</tr>
<tr>
<td>20***</td>
<td>4.06</td>
<td>1.84</td>
<td>3.62</td>
<td>3.54</td>
</tr>
<tr>
<td>10</td>
<td>3.74 ± 0.04</td>
<td>1.80 ± 0.01</td>
<td>3.71 ± 0.11</td>
<td>3.66 ± 0.03</td>
</tr>
<tr>
<td>10***</td>
<td>3.82</td>
<td>1.81</td>
<td>3.97</td>
<td>4.22</td>
</tr>
</tbody>
</table>

Legend:
GR02PR05 = Grade 2 diamond with 5wt% phenolic resin content.
GR02PR10 = Grade 2 diamond with 10wt% phenolic resin content.
*** Experiments carried out in vacuum.
Micrograph showing the infiltration depths in the sample is shown in Fig. 4.22. Only the maximum infiltration height is shown.

**Fig. 4.22:** Cross-section showing the maximum infiltration height after infiltration at 1500 °C for 30 minutes of SiC-coated grade 2 diamond with 10wt% resin at 25MPa.

The infiltration product is fully dense because no pores were evident under the SEM. It seems increasing the resin content helped improve the infiltration depths. Also an increase in open porosity of the green body (low compaction pressure), gave rise to an increase in the infiltration depths. This can be attributed to the increase in pore size thus the pores closed much slower during the fast initial formation of SiC as compared to a case when the pores are a bit smaller. There was some agglomeration that could be seen on the micrographs because two distinct spots can be seen and some areas were a bit darker than the other areas. This was also observed on the infiltrated uncoated diamond.
The agglomeration of the diamond particles observed is suspected to be due to one of the steps incorporated in the preparation of the green compacts. The agglomerates are a carry-over from the sieving process. A -425µm sieve was used to break down the agglomerated powder after the diamond-acetone-phenolic resin slurry was dried. The micrographs of the infiltrated material are shown in Fig 4.23 below.

Fig. 4.23: Micrograph from resin-bonded (10 wt% resin) SiC-coated grade 2 diamond compact infiltrated with silicon at 20MPa (overall vol% composition (Image Tool): Diamond = 39; SiC = 61 and Si =0)
Fig. 4.24: Micrograph and EDS from resin-bonded (10 wt% resin) SiC-coated grade 2 diamond compact infiltrated with silicon at 20MPa (EDS is for the white spots) (overall vol% composition (Image Tool): Diamond = 43; SiC = 57 and Si = 0)

An inhomogeneous distribution of the diamond (dark phase) within the silicon carbide matrix (grey phase) is observed in Fig. 4.24. This can be attributed to the agglomerates formed as described earlier on Page 61. It has been explained when discussing the infiltration of the uncoated diamond preforms that, since the particle size of the diamond used is smaller, the reaction to form SiC seems to consume free silicon completely. This is due to a combination of the large surface area that promotes fast reaction and the small pores with little silicon and thin SiC layer formed through which silicon and carbon migrate short distances to react. Again, no free Si was detected and the white phase seen is suspected to be contamination from polishing or impurities from Si, used as the infiltrant (Fig 4.24).
4.3.3 Mechanical properties of the produced composite.

4.3.3.1 Hardness Tests

Hardness measurements were carried out using the indentation method. This process was fraught with problems because the indenter broke at a load of 35kg, just like in the case of composites made from uncoated diamond preforms (Page 69). The indented material is shown in figure 4.25 below.

![SEM micrograph showing the indent on the composite made.](image)

**Fig. 4.25:** SEM micrograph showing the indent on the composite made.

The indents on the composite are not well defined and formed due to the breaking of the diamond indenter. The load was increased gradually from 15kg to 35kg, but before the 35kg load, no indentation could be formed. From the indentation formed, it was not possible to calculate the fracture toughness of the composite because measuring the
diagonals of the indent would be susceptible to errors and would not represent the true value for the composite. The propagation of the cracks on the composite from the indent is shown in Fig. 4.26 below.

![SEM micrograph showing the propagation of the crack from the indent produced on the composite made.](image)

**Fig. 4.26:** *SEM micrograph showing the propagation of the crack from the indent produced on the composite made.*

The crack is transgranular and this shows that there is a strong adherence of the diamond phase to the silicon carbide matrix.

The wear tests could not be done on the SiC-coated diamond composite as it was assumed that the material will just behave in the same manner as the composite that was produced from uncoated diamond. This was arrived at since all the other properties are almost identical i.e. hardness tests and no porosity from SEM analysis.