Chapter 5: REACTION SINTERING of diamond and silicon powders

In this chapter are presented the results, discussion and conclusion on preparation of the diamond-silicon carbide composite by reaction sintering of diamond and silicon powders. Diamond and silicon were used in their powder state which was admixed prior to sintering. The sintering was carried out in a uni-axial hot-press. The admix route seemed attractive because it is a one-step straightforward process and would reduce production time and costs. This work was performed before the infiltration experiments. Problems were encountered and the infiltration route was ultimately resorted to.

Two most important points to consider:

1. If the diamond should ever graphitize, it should do so to a minimum or should be avoided altogether because non-diamond carbon is not desirable in the final product.

2. The desired SiC binder phase that cements the diamond particles together forms in-situ as a product of the reaction between diamond and silicon. This reaction of diamond and silicon from a powder admix results in a volume reduction leading to formation of pores in the final product.

5.1 Results

Only the D17 diamond powder was used in this part of the work. Different temperature-pressure cycles were used and they are given in Table 5.1.
Table 5.1: Samples produced by admixing using micronizing mill (M) and planetary mill (P). PM indicates those samples for which silicon was pre-milled using a planetary mill and the size-reduced silicon admixed with diamond using a turbular mixer.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Diamond/Si ratio (vol %)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
<th>HEATING RATE (°C/min)</th>
<th>TIME (min) (at T&lt;sub&gt;0&lt;/sub&gt; °C)</th>
<th>PHASES FORMED</th>
<th>DENSITY (g/cm&lt;sup&gt;3&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70:30 (M)</td>
<td>1450</td>
<td>20</td>
<td>30 (1450)</td>
<td>*D+SiC+Si</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>70:30 (M)</td>
<td>1500</td>
<td>20</td>
<td>30 (1500)</td>
<td>D+SiC+Si</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>85:15 (P)</td>
<td>1550</td>
<td>5</td>
<td>30 (1450) 60(1550)</td>
<td>WC+SiC+D</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>85:15 (P)</td>
<td>1550</td>
<td>10</td>
<td>30 (1450) 60(1550)</td>
<td>WC+SiC+D</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>70:30 (P)</td>
<td>1500</td>
<td>10</td>
<td>30 (1420) 60(1500)</td>
<td>SiC+WC+Si+D</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>70:30 (PM)</td>
<td>1500</td>
<td>20</td>
<td>30 (1450) 60(1500)</td>
<td>D+SiC+WC</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>70:30 (PM)</td>
<td>1550</td>
<td>30 (1450) 10(1550)</td>
<td>30 (1450) 30(1550)</td>
<td>D+SiC+WC</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>70:30 (PM)</td>
<td>1450</td>
<td>20</td>
<td>30 (1450)</td>
<td>D+SiC+Si+WC</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>70:30 (PM)</td>
<td>1500</td>
<td>20</td>
<td>30 (1500)</td>
<td>D+SiC+Si+WC</td>
<td>2.2</td>
</tr>
<tr>
<td>10</td>
<td>SPS</td>
<td>1500</td>
<td>20</td>
<td>30 (1500)</td>
<td>D+SiC+Si</td>
<td>2.9</td>
</tr>
</tbody>
</table>

* D = diamond, all others carry the normal chemical formulae/symbols.

*Only densities of 9 and 10 were determined because they were strong enough to handle.

In all the products made from the powder that was mixed using a planetary mill (P) and all that was made from silicon that was pre-milled using a planetary mill prior to mixing with diamond (PM), tungsten carbide contamination is observed. This contamination comes from the planetary ball mill media. The balls and the vessel are made out of WC-Co hardmetal.
Fig 5.1: A DTA pattern obtained on the heating, up to 1450 °C (heating rate of 2 °C/min) of an admix of diamond and Si powder.

A DTA investigation of a mixture of diamond and silicon was carried out to determine reactions taking place in the temperature range 0 – 1450 °C. The DTA-curve shows that up to the melting of silicon, no thermal effect is visible. A strong endothermic effect representing the silicon melting is immediately followed by a strong exothermic effect which represents a chemical reaction between silicon and carbon. During cooling, no observable exothermic effect of solidification of silicon was found suggesting that the silicon was fully consumed by the reaction to form silicon carbide.

5.1.1 **Product obtained using uniaxial hot press**

Sample 1-8 (table 5.1) were soft and highly porous. Their densities were not determined as a result. Sample 9 and 10 were also porous but strong enough to handle and perform density measurements on them. The densities were measured to be 2.2 and 2.9 g/cm³, respectively. For a fully dense material, an average density of 3.5 g/cm³ should be expected for sample 9, assuming all the silicon reacted to form silicon carbide.

Three reaction temperatures were tried, 1450, 1500 and 1550 °C. The heating rate was varied between 5-30 °C/min, and the reaction time was also varied as indicated in the table. SEM micrographs of the products obtained are presented in Fig. 5.2 – 5.6. Because the samples were very soft and couldn’t be polished, they were only lapped to be flat for SEM analysis.

As can be seen, sample 9 has a more cohesive matrix with less porosity than sample 8. Also, silicon appears to have wet the diamond more than in sample 8 (Fig 5.6 vs 5.5). A higher temperature of 1500 °C has produced a better material than a reaction temperature of 1450 °C. Si did not flow around the diamond after it melted because from the micrographs it appears as globules (i.e. confined in one area). This could have been caused by two reasons. Si could still be having a high viscosity at 1450 °C and because this is a powder preform and nor a planar surface as in the case for the wetting angle
studies, the melt flow properties may differ. Fig 5.2 shows that at 1500 °C, Si flows through the sample forming large pools of free Si in the pores of the green body. Another reason could be that for the silicon that is in direct contact with diamond forms SiC around it which then prevents it from flowing upon melting (Fig 5.5). The rate of silicon carbide formation has to be faster than the rate at which the silicon melt spreads at this temperature. Results in chapter 4 prove that silicon carbide forms very fast initially when silicon is still directly in contact with diamond.

Fig 5.2: A typical micrograph in backscatter mode, of a sample after hot-pressing an admix of diamond and silicon from a micronizing mill at 1500 °C (sample 1, Table 5.1).
Fig 5.3: A typical micrograph showing a porous material with WC contamination, of a sample after hot-pressing an admix from a planetary ball mill at 1550 °C (sample 3, Table 5.1).

Fig 5.4: A typical micrograph of a sample hot-pressed at 1550 °C (sample 7, Table 5.1). Milling was done using a turbular mixer. The Si was pre-milled for size reduction using a planetary ball mill. This sample shows an improvement in densification and WC contamination.

Fig 5.5: a) A micrograph typical of a fracture surface of a sample hot-pressed at 1500 °C (sample 8, Table 5.1), b) A close-up on same sample at 5000X.
Fig 5.6: a) A micrograph typical of a fracture surface of a sample hot-pressed at 1500 °C (sample 9, Table 5.1) and b) a close-up of the boxed section in a). Large pores can be clearly seen.

Existence of SiC bridges between diamonds (fig 5.5) prevents the densification of the product once formed. The strong interaction is responsible for the formation of a hard skeleton that cannot collapse under the pressure used in this work. 5.1.2 Phases present in the product detected by XRD are shown in figure 5.7.
Fig 5.7: XRD patterns for samples reacted at 1450 °C for 30 min followed by a heat treatment at 1550 °C for 60 min, a) heating rate of 5 °C/min (sample 3, table 5.1) and b) heating rate of 10 °C/min (sample 4, table 5.1).
5.1.2 Product obtained from powder mixed using a turbular mixer and hot pressed by SPS.

Fig 5.8: An example of a microstructure of a product obtained through pressing with an SPS machine in Germany showing wetting by silicon but non-densification.

Fig 5.9: An example of a microstructure of a product obtained through pressing with an SPS machine showing lack of silicon in areas of porosity (non-densification). Diamond (black phase) = 73 vol%, SiC (grey) = 6 vol%, Si (white) = 21 vol%.
From the micrographs above, it is clearly visible that silicon wets the diamond, however, it does not reach or flow to reach all pores. Free silicon persists into the final product. This could be a reiteration of the fact that a fast formation of SiC around the silicon where silicon is in direct contact with diamond leads to encapsulation/containment of the silicon and prevents it from flowing around the diamond.

5.2 Discussion

As can be seen from the micrographs of samples produced from powder admix obtained from planetary ball-mill (fig 5.5), a lot of tungsten carbide (WC) contamination exists. This WC contamination cannot be removed. An alternative mixing (using turbular mixer) eliminated most of the WC contamination from the powder mix because it is a much gentler process. The WC found here is from the pre-milling of the Si for size reduction using a planetary ball mill. The micronizing mill was found to result in inhomogeneous mixing, the powder had to be taken out, stirred and put back in the vessel several times until a homogenous mixture could be obtained. The vessel and balls used in the micronizing mill were both made from a plastic material. The balls do not rotate, they just vibrate about a point and this could be the reason for the inhomogeneity.

When 15 vol% Si was used, no free Si was observed in the final product. 30 vol% Si content, under the same hot-pressing conditions, resulted in free Si phase in the final product.

The products obtained were highly porous. They were also very soft, with a maximum Knoop macro-hardness value of 11 GPa (sample 9, table 5.1), target hardness being greater than 35 GPa. The low hardness is largely due to non-densification of the products.
The diamond-silicon carbide composite was difficult to densify because of the strong skeleton that forms accompanying the SiC formation. Silicon carbide forming on adjacent diamond grains can grow and join them forming a strong bridge structure.

Upon reaching Si melting point, the melt cannot flow around and wet the diamond grains most probably because it is hindered by the SiC that forms around it on its surface and hinders its spreading. This surface SiC may be formed by gas phase reactions. The result is an enclosure of the melt which leads to “bare” diamonds where Si can not reach them.

The wetting angle measurements (section 4.1) indicate a good wetting of diamond by silicon. It should be expected hence that after it melts, Si should be able to flow around the diamond grains because of the good wettability of the system. However, use of silicon powder instead of wafers increases the silicon affinity to oxygen. The silicon surface is covered by an oxide (SiO$_2$). This oxide layer is the one that initiates a chain of reactions to form SiC on the surface of silicon. It first starts by reacting the diamond to form CO and SiO. CO upon reaching the silicon surface reacts to deposit SiC there and release SiO which reacts with diamond to produce more CO that deposits more SiC onto the silicon. Eventually, the silicon is enclosed in this SiC and cannot flow around to wet the diamond particles.

\[
\begin{align*}
\text{SiO}_2(s) + \text{Si} &\rightarrow 2 \text{SiO}(g) \\
\text{SiO}_2(s) + \text{C} &\rightarrow \text{CO}(g) + \text{SiO}(g) \\
\text{CO}(g) + \text{Si} &\rightarrow \text{SiC}(s) + \text{SiO}(g) \\
\text{SiO}(g) + \text{C} &\rightarrow \text{SiC}(g) + \text{CO}(g)
\end{align*}
\]

It is possible however that even though the DTA (fig 5.1) does not quite give a pronounced peak for the SiC formation before the Si melting temperature, the solid state reaction to form SiC may be occurring gradually as the temperature approaches silicon melting point, slow enough not to produce an intense exothermic peak. However, once the Si starts to melt (which is an endothermic process), it enhances the exothermic reaction (of SiC formation). As a result, only then is an intense peak observable.

\[ C + Si \rightarrow SiC \quad \Delta H = -74.11 \text{ kJ/mol} \]

\[ Si \ (s) \rightarrow Si \ (l) \quad \Delta H = +50.18 \text{ kJ/mol} \]

The SiC bridges that form in this material are strong, SiC is a covalent structure. They cannot be caused to collapse under the pressures employed. This reaction sintering therefore requires application of an external pressure to help densification.

From calculations made (in Table 5.2 below), it can be seen that the reaction sintering route is connected with volume reduction and hence will always result in residual porosity in the final product unless an additional step can be performed where these pores are re-infiltrated with silicon or real shrinkage takes place. This shrinkage can only take place due to sintering of SiC and diamond, but for this process to take place, much higher temperatures and pressures are necessary. Open porosity is required for infiltration to
take place. So, whatever attempts are made to re-infiltrate the resulting porous structure will not eliminate entirely the porosity. This means that this problem is almost insolvable under the pressure conditions employed.

Table 5.2: Some calculations (molar volume) of the changes in volume when the reaction sintering route and the infiltration route are employed in the in-situ production of SiC binder phase for the diamond composite.

\[
C + Si \rightarrow SiC
\]

<table>
<thead>
<tr>
<th>C source</th>
<th>METHOD</th>
<th>C volume (cm(^3)/mol)</th>
<th>Si volume (cm(^3)/mol)</th>
<th>SiC volume (cm(^3)/mol)</th>
<th>(\Delta V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Admix</td>
<td>5.45</td>
<td>12.0</td>
<td>12.5</td>
<td>-28.4 %</td>
</tr>
<tr>
<td></td>
<td>Infil</td>
<td>5.45</td>
<td>0</td>
<td>12.5</td>
<td>+129 %</td>
</tr>
<tr>
<td>Diamond</td>
<td>Admix</td>
<td>3.41</td>
<td>12.0</td>
<td>12.5</td>
<td>-18.8 %</td>
</tr>
<tr>
<td></td>
<td>Infil</td>
<td>3.41</td>
<td>0</td>
<td>12.5</td>
<td>+266 %</td>
</tr>
</tbody>
</table>

Densities (g/cm\(^3\)): G = 2.2; D = 3.51; Si = 2.33; SiC = 3.18

In an attempt to hopefully crush the strong porous structure that forms during the solid-state reaction, application of a higher pressure was used. An admix was made, similar to the previous ones using a turbular mixer, pressed and sintered using an SPS technique (Fig 5.8 – 5.9). A pressure of 50 MPa was used. Si seemed to have wet the diamond and the SiC-bridges are nonexistent. The density of the final material was determined by archimedes principle to be 2.84 g/cm\(^3\). This has however been a great improvement from the 2.2 g/cm\(^3\) determined for the hot pressed product.

The use of a low-temperature melting eutectic alloy was then explored (Chapter 6) as an alternative because of the hypothesis that if the melting takes place at a lower temperature, then wetting and densification will occur well before the intensive reaction of Si with diamond kicks in.
5.3 Conclusions

An effective way to mix diamond and silicon was found by using turbular mixer. This method produces less contaminated products and homogenous mixing.

Lower silicon content leads to its premature depletion and not all diamond is covered by silicon upon its melting. The resulting material is porous and lacks in hardness, which renders it useless in the ultrahard materials applications.

The products obtained by this route are highly porous with the lowest apparent porosity of 35 % and the highest Knoop macrohardness value of 11 GPa.

The reason for high porosity is connected to the strong interaction of silicon with diamond. This solid-state reaction results in the formation of SiC-bridges which hinder the wetting of the diamond by silicon after it melts. Also due to this strong SiC bridges, densification is difficult, and the resultant material is porous.

Results and calculations reveal that starting off with an admix will always result in porosity in the final product if the densification due to external pressure is not fast enough to compensate for volume shrinkage.

The use of a low-temperature melting alloy might help separate the intensive reaction from the wetting and densification steps.