CHAPTER 2: LITERATURE REVIEW

2.1 Materials

Diamond with a Knoop hardness value of 100 GPa [1] is the hardest material known to mankind. Because of this, it is a highly attractive material for industrial use as cutting tool, wear parts and drilling material. However, it is difficult to cut and shape for various industrial applications. The solution hence is to make polycrystalline diamond materials. This does not only allow shaping, which some authors refer to as “formable diamond”[2], it also increases the fracture toughness of the diamond because of the introduction of a secondary phase (called the binder phase) to consolidate the diamond crystals, which on their own are brittle. Metallic binder phases (especially copper) were initially popularly used to bind diamond particles together, however they were later found to be catalyzing the graphitization of diamond under high temperatures (> 700°C) [2] which limited applications thereof.

Silicon carbide was found to be an excellent binder phase and since its discovery due to its attractiveness, it has gained wide popularity among researchers. Apart from rendering the product with greater fracture toughness, SiC is also highly compatible with diamond. It exhibits the same cubic crystal structure as diamond and therefore together they form a coherent “interlocking” matrix where the silicon carbide is formed from the diamond in-situ.[3] The thermal expansion coefficient of SiC also closely matches that of diamond. The resultant composite material exhibits high thermal conductivity due to the individual conducting nature of both diamond and silicon carbide combined with the fact that together they form a highly coherent interlocking composite. The material hence finds use in thermal applications, for example as heat conductors [3] as well as heat conducting cutting tools. SiC does not react with diamond and is also highly stable at high temperatures enabling diamond-SiC composites to be applicable at higher temperatures than their metal-containing counterparts. Where SiC was formed in-situ from a reaction between silicon and diamond, the application temperature is limited to the melting
temperature of the unreacted silicon (1400°C) [1]. It is paramount therefore, to react most of the silicon. Also because silicon is the softest phase of the three, the lesser there is of it, the higher the hardness of the product.

Different procedures have since been followed on how this binder phase can be introduced into a diamond preform. Basically there are two synthesis routes for the diamond-SiC composites in existence. One is the sintering of an admixed powder of diamond and silicon and the other is the infiltration of diamond by molten silicon followed by reaction. In both procedures an in situ reaction between diamond/carbon and silicon to form SiC takes place. It is assumed that it is the carbon on the diamond surface that gets involved in the reaction and by so doing decreases surface defects and strain on the diamond surfaces [4]. The reaction-sintering route necessitates high pressure application to ensure compaction and elimination of porosity that forms as the reaction proceeds. It is of importance to note that if the reaction proceeds without an external re-supply of the Si melt, voids are produced within the body [5] or high pressure has to be used. Subsequent reaction between diamond/carbon and silicon then forms SiC which forms the binding phase. This SiC formation is reported to start immediately after the melting of silicon [6].

Mostly high pressure-high temperature conditions have been used in manufacturing these composite materials. It is only recently that attempts are being made to produce said materials using low or ambient pressures.

Some researchers have reported success in making the composite material following the reaction-sintering route [7]. They milled diamond powder together with silicon powder and the latter is transformed into its amorphous form during the process. When the mixture finally sinters, under high-pressure high-temperature conditions (5-8 GPa and 1400°C-2000°C), nano-sized SiC is formed and the authors[4] claim that the overall material has a better fracture toughness than that obtained via the infiltration technique due to the nanostructure of their SiC compared to the micron size SiC that forms in the infiltrated samples (Fig 2.1). Their hardness values however are less than those of the
infiltration-produced counterparts, which J. Qian et al. [4] attributes to the smaller residual strain of the SiC in infiltrated products.

![Nanostructured Diamond-SiC Composites](image)

**Fig. 2.1:** The relationship between the fracture toughness of the diamond-SiC composite and the grain size of its matrix. [8]

From this it then follows that depending on the ultimate use of the material, either the hardness or the fracture toughness can be maximized by properly choosing the synthesis route. The infiltration technique is also attractive because much lower pressures can be employed during this technique [3]. The advantage of the infiltration technique as stated by J. Qian et al. [9], is that the liquid phase fills the pores in the diamond skeleton and results in a dense material without necessarily requiring high pressure.

Other methods that have been tried in the manufacturing of these diamond-SiC composites are shock-compaction technique [10,11] and the static-pressure methods [11]. Both methods did not yield in very good products as the microhardness values obtained were less than satisfactory. [12] It was found by M. Ohkoshi et al. [10] that the diamond grain boundaries in the shock-compacted microstructure consisted of amorphous carbon.
All the above procedures except the infiltration method have one thing in common, high pressure. Because diamond graphitizes easily under low-pressure, researchers mostly confined themselves to fabricating these diamond composites under the diamond stable conditions. Also, because the melting point temperature of silicon decreases with increase in pressure, high pressure use allows for infiltration at lower temperatures, which further ensures no graphitization of the diamond. The use of low pressure however will help realization of composites of large sizes and complex shapes. There have been several attempts in producing these materials under the diamond’s non-stable low pressure region and one of them was using the Hot Isostatic Pressing technique (HIP technique).[13] A pressure of 50 MPa was used and the resulting composite had no graphite in it and was >90% dense. Gordeev et al [14] of Skeleton Technologies on the other hand, produced a fully dense material by pressureless infiltration of pre-graphitized green compacts. This is proof that the diamond-SiC composites can be successfully made under the diamond unstable conditions without necessarily ending up with graphite in the final product.

2.2 Infiltration theory

For infiltration to take place, the porous preform (i.e. the structure to be infiltrated) should have pores which are open and interconnected, i.e. should be at least 10% porous [15] to ensure that the liquid infiltrating into the preform (i.e. the infiltrant) reaches all pores in the preform and that a final fully dense product is obtained (Fig. 2.2). The infiltrant is placed either on top of or under the porous compact (preform) to be infiltrated. The assembly is heated up and upon reaching the melting temperature of the infiltrant, the liquid melt starts to fill the pores of the preform. If all pores have been filled, the system is said to be fully infiltrated and if it partly filled it is termed partially infiltrated.
Surface chemistry becomes specifically interesting when dealing with powder systems because of the high surface/mass ratio they possess. The surface atoms are highly active and tend to change the surface composition compared to the bulk. Change in the surface chemistry may affect the wettability of a system enormously which ultimately impacts on infiltration. It is therefore of paramount importance to study and characterize the surface(s) for infiltration well before it can be performed.

Infiltration can take place in two different ways, with interaction between the melt and the preform or without interaction. For an infiltration system without interaction the wetting behavior of the system plays a major role in determining the success of the infiltration. In the case of an infiltrating system with interaction however, the interaction (i.e. the reaction between the infiltrant and the preform) together with the wetting behavior are the main parameters that determine the infiltration of such a system.

First a non-reacting infiltration system will be analyzed more in detail.
2.2.1 Non-reactive infiltration

When a porous preform has to be infiltrated with a liquid melt, the wettability of the preform by the liquid is highly important because only if the liquid wets the solid phase will spontaneous wicking of the liquid into the pores of the preform take place. In addition to this, wetting may even cause some compression to occur between particles, driving the system to greater densification. For contacting spheres, the compression is greatest when $\gamma_{LV}\cos\theta$ is large and the volume of liquid is small [16] (Fig 2.3).

Fig 2.3: Juncture of interfacial tensions for a liquid on a solid surface and cases of non-wetting (a) and wetting (b).

In principle, a system with $\theta < 90^\circ$ is classified as wetting and that with $90 < \theta < 180^\circ$, as non-wetting. [16]

For a pressureless non-reactive infiltration, the height of infiltration (assuming cylindrical pore channel) that can be obtained purely from capillary force is

$$\delta H = \delta P/\rho g = 2\gamma_{LV}\cos\theta / R_c\rho g \quad (2.1) [16]$$

where:
\begin{align*}
\delta H &= \text{height risen by liquid} \\
\delta P &= \text{internal pressure} \\
\rho &= \text{density of the liquid} \\
g &= \text{acceleration of gravity}
\end{align*}
Rc = the radius of the pore
\( \gamma_{LV} \) = surface tension
\( \theta \) = contact angle/wetting angle

It can be deduced from equation 2.1 that fine pores will suck the liquid to a greater extend than large pores.

The average laminar flow velocity \( (v) \) of liquid in a cylindrical capillary is given by

\[
v = \frac{\gamma_{LV} \cos \theta R_c}{4 \eta L}
\]  

(2.2) [16]

Where:
\( \eta \) = the viscosity of the liquid
L = the length filled by the liquid

From equation 2.2, it can be seen that the rate at which the liquid will penetrate the preform will increase if the viscosity of the liquid is lowered (which generally can be done by increasing the infiltration temperature), when the surface tension increases, as well as when preforms of coarse particle size are used, which will result in large pore radii.

Washburn equation [17] goes further to predict the infiltration height taking into account the time allowed for infiltration to take place:

\[
x^2 = \frac{\gamma_{LV} \cos \theta}{2 \eta} R_c \cdot t
\]  

(2.3)

Where:
\( x \) = infiltration depth
\( R_c \) = pore radius
\( t \) = infiltration time
\( \eta \) = viscosity
\( \gamma_{LV} \) = surface tension
\( \theta \) = contact angle
The term \( \frac{\gamma_{LV} \cos \theta}{2\eta} \) is called the penetration coefficient. According to the Washburn equation, the longer the time allowed for infiltration, the greater will be the infiltration depth.

For systems consisting of tortuous non-uniformly sized pores like powder preforms, the total permeability can be written in terms of particle size and porosity, Washburn equation then becomes [18]:

\[
\ell^2 = \frac{12D_p \varepsilon^2 \gamma_{LV} \cos \theta}{150(1 - \varepsilon) \eta} t
\]

(2.4)

Where: \( \ell \) = infiltration length
\( D_p \) = primary particle size
\( \varepsilon \) = powder bed porosity

If the system is non-wetting however, no spontaneous infiltration will occur, and contrary to a wetting system, a liquid that is non-wetting tends to force particles apart. An external pressure has to be applied in order to induce infiltration in this type of a system. This pressure has to be greater than a certain value referred to by O. Garbellini et al [19] as the minimum capillary resistance of the preform to the penetration of the liquid melt into the largest interspaces. Darcy’s law [20] states that:

\[
h^2 = \frac{2k}{\mu(1 - V_p)} \Delta P
\]

(2.5)

Where: \( h \) = infiltration height
\( k \) = intrinsic permeability
\( t \) = infiltration time
\( \mu \) = viscosity of liquid melt
\( V_p \) = particle volume fraction of packed sample
\( \Delta P \) = pressure drop in the liquid
According to Darcy’s law, a plot of $h^2$ against pressure (fig 2.4) gives a straight line and an indication of the amount of pressure necessary to initiate an infiltration process.

![Fig 2.4: An illustration of Darcy’s plot of infiltration height vs pressure.](image)

It is a great challenge to predict fairly the infiltration depth and the speed of infiltration for a non-reactive system and even more challenging for a reactive system.

### 2.2.2 Reactive infiltration

Adding onto the complexity of non-reactive infiltration systems is the reactive infiltration. Apart from the wettability of the system, the rate of the product formation plays a major role.

Some factors that are important in reactive-infiltration are:

1. pore size distribution
2. pore shape
3. viscosity of melt
4. the heat of reaction accompanying the product formation
5. the rate of reaction
6. wettability
7. temperature and
8. external pressure

1. Pore size distribution
It is clearly demonstrated that fine pores wick up liquid melt to a greater extent than coarse pores (equation 2.1) however, the fine pores possess larger surface area than the large ones. The combination of large surface area to pore volume and slow pore-filling in fine-pore structures is lethal to a reactive-infiltration system. The large surface area means that the reaction proceeds much faster to minimize the energy of the system. The faster the reaction products are formed, the faster the pores are diminished, and the more difficult penetration becomes. An increased external pressure may be applied to force the infiltrant through the preform once it is in liquid form. There is a need therefore to determine the optimum pore size that can be fully infiltrated prior to blockage by product formation. The porosity should be adequate to accommodate the product as it forms as well as any volume expansion of residual infiltrant upon cooling if the melt exhibits an anomalous phase transition (i.e. expands on cooling), as is the case with a silicon melt [21].

2. Pore shape
Pores in a powder preform are tortuous and enlarge and narrow along their length. Because of the complexity of the pore shapes in preforms, and their variation within one preform, it is difficult to get a representative pore shape in any preform. However, the use of a pore shape factor [22] may reduce the error associated with this problem.

3. Melt viscosity
Obviously a highly viscous melt will be more difficult to wick up a porous preform even if the wetting is considered good between the two. However generally, high temperatures can be employed to lower the viscosity of a melt, but in some systems like the diamond-Si case, the temperature cannot be increased to more than 1600°C under low pressures because it poses the danger of graphitizing the diamond. So, the refractoriness of the preform has to be determined in order to establish how high the temperature can be raised to reduce the melt viscosity.
4. The heat of reaction
Depending on whether the reaction taking place is of endothermic or exothermic nature will affect the infiltration in some way. For example, the formation of silicon carbide from carbon and silicon is exothermic ($\Delta H_{298}^{\circ} = -(69-73)\text{kJ/mol}$).[23] This means that once SiC starts to form, local temperature starts to increase which further propagates reaction. The degree of temperature rise depends on the type of carbon source. Fitzer and Gadow reported a 600K temperature rise for natural graphite being reacted at 1700K.[23] The accelerated product formation results in faster pore closure and greater difficulty to further infiltrate the preform.

5. The rate of product formation
Interconnected pores should be maintained until full infiltration. Therefore it is desired that the infiltration and reaction can be separated. This is not possible for all reactive infiltration systems, for example in the diamond-silicon infiltration system the reaction occurs simultaneously with infiltration and the rate of reaction is very fast. Fast formation of product results in blocked pore channels and further infiltration cannot take place. A way of retarding the reaction so that the rate of infiltration far surpasses that of product formation would help alleviate this problem.

6. Wettability
Good wetting is of paramount importance in assisting or enhancing the extent of infiltration. A liquid exhibiting a low contact angle readily fills open pores. An external pressure may only be used to enhance the rate of infiltration if a system exhibits good wetting.

7. Temperature
In general, infiltration has to be carried out at temperatures higher than the melting point of the infiltrant (Si) but less than the softening or deformation temperature of the porous preform. Temperatures much higher than the infiltrant melting temperature will decrease the melt viscosity and hence expedite the pore-filling process. For example, the melting point temperature for silicon is 1410°C[24], high quality diamond starts graphitizing
under ambient pressures at \(\sim 1700^\circ C\) [25] under controlled atmosphere, infiltration by silicon therefore is usually carried out at \(1500^\circ C\) [24]. It should be noted that graphitization may be induced at temperatures lower than \(1600^\circ C\) in the presence of surface impurities or defects even if the atmosphere is kept inert depending on the type of impurities or defects.

8. External pressure

There exists a pressure differential at the liquid front during infiltration which determines whether the infiltration will be spontaneous or will require application of external pressure in order to “force” the liquid into the preform. External pressure may also be used just to increase the rate of infiltration and also to help the infiltrating melt to reach smaller pores in the preform. It can be deduced from the work of E.A. Ekimov et al [12] that a threshold of externally applied pressure (7.7 GPa) is reached beyond which no real improvement in infiltration depth is achieved for the diamond-SiC system.

In a reactive infiltration system, further complications exist due to the volume change accompanying the reaction. Looking at a case where graphite reacts with silicon, for example, the volume occupied by the carbon atoms more than doubles as graphite is converted to SiC.[5]

The greatest challenge presented by this is that interconnected porosity has to be maintained throughout until full infiltration has been attained. This means that there exists an optimal preform pore diameter that can result in full infiltration, large enough to accommodate the volume expansion of the solid phase during reaction and maintain open channels for continued infiltration. Compounding to this, in the diamond-silicon system, is the aim to have as little free silicon in the final product as possible. If too large pores exist then it is very difficult to achieve this, there will always be a high probability of ending up with free silicon in the final product. Free silicon is undesirable as it compromises the mechanical properties and high temperature characteristics of the product. The presence of free silicon limits the upper use temperature of diamond-silicon carbide composites to below the softening/melting temperature of silicon.
It is accepted that in a non-wetting system, the largest pores are filled first and require application of external pressure. In wetting systems however, like the one in consideration here, the melt will first be drawn into the smallest pores decreasing the surface/volume ratio with time. It then follows that in a wetting reactive carbon/silicon system Si melt fills the fine pores first, further encouraging pore closure as reactions proceed much faster in fine pores due to their high surface area.

### 2.3 Carbon-silicon interactions

#### 2.3.1 Carbon-silicon reaction

It has been widely accepted that the reaction between diamond and silicon starts on the surface of the diamond [26,27] and results in formation of β-SiC. It was found that there exists an orientation of the formed SiC relative to diamond, independent of whether high pressure or low pressure was used.[26-28]

Surface defects have been described to play an important role in the initiation of the reaction.[26,27] It has been proposed by C. Pantea et al.,[26] that SiC first starts to form by nucleation at random places throughout the structure and then grows both laterally and vertically. SiC islands are formed and as they grow, they eventually coalesce and form a uniform cover on the diamond surface. Once the surface of the diamond is fully covered, growth of the SiC product then becomes controlled by the diffusion of the reacting species, carbon and silicon, through the SiC barrier to the reaction front. In other literature [29], a discontinuous layer of β–SiC has been observed for short periods of reaction time (i.e. less than 150 sec). This discontinuity may be evidence of the initial SiC islands formation proposed by C. Pantea et al.[26]

This means that with time there will be a spatial separation of the reactants by the formed product. For the reaction to continue, these reactants have to somehow find their way to
each other in order to continue forming the product and this will only be by migration through the SiC product barrier. Opinions only differ with respect to the actual mechanism of how the reactants migrate to the reaction front.

Pampuch et al [30], Sawyer and Page [31] and Ness and Page [32] proposed that the growth of SiC from graphitic carbon takes place in a solution-reprecipitation manner. These authors assume that carbon dissolves into molten silicon and SiC precipitates when the solution is supersaturated. Highest dissolution of carbon in silicon is believed to be at the reaction front where specimen temperature is at its peak due to the exothermic nature of the reaction and the supersaturation is believed to exist in the cooler regions away from the reaction front [30]. These authors further proposed a model suggesting a periodical carbon-dissolution and periodical supersaturation of liquid phase with respect to SiC. Independent research by Zhou and Singh [33] revealed random SiC precipitates in the silicon phase which could be proof of carbon that dissolved in liquid phase and got carried away much deeper into the silicon phase and eventually precipitated as SiC, most probably during cooling. This observation can be used as proof to support this solution-precipitation theorem.

Following the general theory of the final SiC growth being determined by a diffusion-controlled mechanism, several studies have been undertaken to investigate the diffusion mechanism of carbon and silicon through SiC. Of interest to this research work is the diffusion through the cubic polytype of SiC, β–SiC because this is the phase that is formed under the conditions employed for all experimental work in this study. No hexagonal type of SiC (α-SiC) was formed in all the experiments carried out.

A general acceptance for the diffusion of silicon and carbon through β-SiC has been that both species migrate via a vacancy mechanism, but at different rates, and that carbon diffuses faster than silicon due to its smaller atomic size, hence it accounts for most of any further conversion to silicon carbide [34]. The diffusion constants of carbon and silicon in SiC are given in figure 2.5.
In other literature data [31] the assumption is made that an internal electric field is set over the reaction-formed SiC layer and that it drives the diffusion of carbon ion vacancies across the SiC layer, and that this is the rate limiting step. The common factor in the above propositions is that the migration of the carbon species is the one that seems to be rate-controlling.

William B. Hillig [5] however has a slightly differing point of view. He suggests a coupling of the carbon and silicon fluxes across the SiC barrier. His argument is that if carbon transport is faster than that of silicon, the carbon at the carbon-SiC interface will become depleted. An observation of an intact interface implies that silicon is also transported in the opposite direction.
Hase et al [36] found that the β–SiC formation process during reaction-sintering depends on the microstructure of the carbon particle and the particle size. β–SiC formation was found to be greatest in less crystalline carbon and in fine-powdered reactants.[36,37] Fortunately the degree of crystallinity in carbon powder decreases as the carbon particle size decreases, therefore these two act synergically to enhance the reaction. It would be expected therefore that when silicon reacts with a carbon-coated diamond skeleton, the β–SiC formation will be fast initially when the silicon reacts with the amorphous carbon, and then slow down once it reaches the diamond surface which is highly crystalline. Increasing the reaction temperature has been found to increase SiC content in the final composite.[6]

The literature on the actual kinetics of the reaction between diamond and silicon was done only recently by C. Pantea et al [26] under high pressure-high temperature conditions. In this literature it was found that the rate of reaction between diamond and silicon is very fast, so fast that it cannot be explained by the self-diffusion activation energies in literature. The conversion of reactants to SiC is very fast initially but slows down with time with insignificant increase in SiC formation after about 20 minutes (Fig 2.6). The reaction kinetics had however been studied using powder. Powder contains more grain boundaries than the single crystals used for the self-diffusion experiments. Presence of a large number of grain boundaries could have enhanced the diffusion of the reacting species, resulting in the fast SiC formation observed in this study.
Fig 2.6: Plot of the degree of reaction of diamond and silicon, α, vs time. Solid line represents the best fit of the Avrami-Erofeev equation to exponential data for the (111) reflection. The insert shows error bars in reaction rate, k, determination for the different reflections of SiC.[26]

There is much greater literature coverage on the kinetics of the reaction between non-diamond carbon and silicon. Hong Zhou and Raj Singh [33] studied the reaction kinetics of a glassy carbon with silicon and also observed extremely fast initial reaction rates. The study concluded that the overall rate followed a fourth-power rate law. In table 2.1 is a presentation of an overview of the SiC thickness values reported for reaction time of 180 minutes at 1430, 1475 and 1510°C reaction temperatures. These values will be compared to those obtained in this PhD work.
Table 2.1: Maximum SiC thickness values obtained by Zhou and Singh [33] after a 20- and 180-minutes reaction times at different reaction temperatures.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Thickness (µm)</th>
<th>20 min</th>
<th>180 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1430</td>
<td>~8</td>
<td>~10</td>
<td></td>
</tr>
<tr>
<td>1475</td>
<td>~8.5</td>
<td>~9</td>
<td></td>
</tr>
<tr>
<td>1510</td>
<td>~8.5</td>
<td>~11</td>
<td></td>
</tr>
</tbody>
</table>

Observed from these results is that for the temperature range 1475-1510°C, the thickness of the SiC layer increases with increase in reaction time and that at lower temperatures (1430°C), SiC thickness seems to grow fastest initially and reach its maximum. Further dwelling at the reaction temperature doesn’t seem to increase this SiC thickness observably.

Infiltration of a carbon/diamond preform with silicon leads to a volume expansion while a reaction-sintering route results in volume reduction and hence possibility of pores in the final product if produced under low pressure. Using equation 2.6 as an example, 5.5 ml/mol graphite increases to 12.5 ml/mol SiC during reaction-infiltration, while the combined 17.1 ml/mol reactants decreases to 12.5 ml/mol SiC during reaction-sintering.

\[
\text{Graphite(s) + Si(l)} \rightarrow \text{SiC(s) + heat \hspace{1cm} (2.6) [5]}
\]

\[
5.5 \text{ ml/mol} + 11.6 \text{ ml/mol} \rightarrow 12.5 \text{ ml/mol}
\]

This therefore means that for composites being reaction-sintered, an ultra-high external pressure is necessary to densify the product. Chiang, Messner and Terwilliger stated that without continuous infiltration about 25% porosity should result from reaction-sintering process. [38]
2.3.2 The wetting of carbon and/or diamond

Wettability is a very sensitive characteristic in an infiltration system. It is significantly affected by small changes in many factors such as composition, type and amount of impurities, surface roughness and the crystal orientation of the solid phase (in this case carbon or diamond). It plays a highly significant role in infiltration because it is an indication of the ease of penetration of a porous preform by a particular liquid/melt.

Both carbon and SiC generally show a good equilibrium wetting by liquid silicon as has been reported (Table 2.2). This therefore means that wetting is not of great concern in the system under consideration here, unless if there exist surface contaminations. Wetting is highly sensitive to surface contaminations. Usually for reactive infiltration systems, the reactions themselves increase surface tension and infiltration is therefore enhanced by this.

Table 2.2: The reported wetting angles of different carbons and SiC by silicon.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TEMPERATURE</th>
<th>CONTACT ANGLE (°)</th>
<th>LITERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitreous carbon</td>
<td>Equilibrium</td>
<td>10-50</td>
<td>O. Dezellus[39]</td>
</tr>
<tr>
<td>Graphite</td>
<td>Equilibrium</td>
<td>5-15</td>
<td>O. Dezellus[39]</td>
</tr>
<tr>
<td>Polycrystalline pyrolytic graphitic</td>
<td>1482</td>
<td>5-23</td>
<td>R. Pampuch[30]</td>
</tr>
<tr>
<td>SiC</td>
<td>1482</td>
<td>30-41</td>
<td>R. Pampuch[30]</td>
</tr>
<tr>
<td>SiC</td>
<td>1430</td>
<td>38.5</td>
<td>Zhou &amp; Singh[33]</td>
</tr>
</tbody>
</table>

The vastly studied systems of carbon/silicon have indicated that these systems exhibit a final equilibrium wetting angle consistent with that of silicon carbide/silicon systems (30°-45°). O. Dezellus et al.[39] suggests that silicon does not wet carbon and that the final wetting exhibited by this system is only a result of the SiC interface formation. If this is true, it implies that the rate at which silicon spreads on the carbon (i.e. the wetting angle) is governed by how fast the reaction to form SiC takes place at the triple point.
Fig 2.6: The formation and lateral advancement of the SiC layer controlling the spreading of molten silicon as it happens.

Other studies have found much lower values of the wetting angle between carbon and silicon melt (Table 2.1). It has also been found that the wetting behavior varies with different types of carbon, the surface roughness and porosity of the solid being wetted. Fitzer and Gadow [23] studied the reactivity of different carbons with liquid silicon and found that glassy carbon is quickly protected by a thin layer of solid SiC, a “vehement” reaction was observed for natural graphite, while an “extremely vehement” reaction was observed for pyrolytic carbon. If the rate of spreading of the liquid phase is indeed controlled by the rate of reaction at the triple point, it means that the faster the system reacts the faster it will reach its final wetting angle but the characteristic equilibrium wetting angle will not change.

### 2.4 Infiltration behaviour of carbon preforms

A system in which infiltration of carbon (diamond/graphite/glassy carbon/other) by silicon is taking place is classified as a reactive-infiltration system. This system presents some challenges in that a reaction happens simultaneously with infiltration. Once the silicon melt comes into contact with the preform, the reaction between the silicon and carbon initiates and silicon carbide starts building up. The silicon carbide that forms is in its solid state and has a specific volume greater than that of the solid carbon preform and
therefore results in expansion. Table 2.3 shows by how much the volume of a graphite preform and a diamond preform will expand during their infiltration with silicon.

Table 2.3: Theoretical volume expansion of carbon preforms upon infiltration with silicon melt as it reacts as follows: C -> SiC

<table>
<thead>
<tr>
<th>C source</th>
<th>Molar Volume (cm³/mol)</th>
<th>SiC molar Volume (cm³/mo)</th>
<th>Volume change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>5.45</td>
<td>12.5</td>
<td>129</td>
</tr>
<tr>
<td>Diamond</td>
<td>3.41</td>
<td>12.5</td>
<td>266</td>
</tr>
</tbody>
</table>

The values in the table above were calculated using the densities (g/cm³):
Graphite: 2.2
Diamond: 3.51
Si: 2.33
SiC: 3.18

The expanding solid product formation as a result reduces the porosity of the preform and slows down the infiltration process with time by reducing the rate of the entry of additional melt and may ultimately result in blockage of the pores and premature termination of the infiltration (prior to full infiltration of the preform). This phenomenon of pore-closure is often referred to as the “self-stop” phenomenon [12] or “reaction choking” [40]. The main advantage of reactive-infiltration however, is that it offers lower processing temperature, shorter processing times, and the possibility of fully dense products and near net-shaping without necessarily requiring application of an external pressure.[29] A reaction enhances the wetting and hence does not necessitate application of external pressure. Tailoring of the preform to having porosity just enough to accommodate expansion can make a near net-shape product a possibility.

Infiltrating preforms with large pores results in a product containing free silicon. Residual silicon in the final product is undesirable because it limits mechanical properties and the upper use temperature. Also failure flaws have been reported [40] to appear to initiate at and propagate along the Si-SiC interface when infiltrating with silicon-
molybdenum. Zhou and Singh [29] stated that the strength and elastic modulus in Si/SiC composites dropped at temperatures above $1410^\circ C$ (i.e. above the melting point of pure silicon).

In an attempt to completely consume free silicon in SiSiC materials, some researchers have resorted to employing silicon alloys that form stable refractory silicides.[38,40] Any remaining free silicon is precipitated out as a silicide. However, the use of alloys comes up with other complications due to the introduction of an extra phase into the system, for example, the compatibility of the thermal properties of the extra phase with those of the composite, its effect on the mechanical properties of the final product, etc.

Attempts to infiltrate fine-pore preforms have not proven successful. E.A. Ekimov et al [12] tried the infiltration technique on nanocrystalline diamond using ultra-high pressures and temperatures (7.7 GPa, 1400-2000$^\circ C$) but still found they were limited by the reaction choking, realizing a maximum infiltration depth of 2 mm. It can be inferred from this that in cases where a fine-grain composite material has to be made, a different route has to be adopted because regardless of the high pressures that may be used, the reaction is still so fast that it limits the realization of full infiltration. J. Qian et al [9] followed a different synthesis route based on high-energy ball milling. Their approach although successful in that a fine grain composite was made, still required the use of high pressures and temperatures to avoid graphitization of the bare diamond, and to reduce void volume. Reduction in grain size is highly attractive because with the smaller grain size higher hardness values can be achieved. Nanocomposites in their application as cutting and finishing tools are expected to give a better quality of cutting edge.[12]
2.5 Project motivation

The possibility to produce SiC-diamond composites under low pressures without the danger of having graphite in the final product makes this composite material highly attractive. With employment of low pressure the cost of production is enormously reduced because the dies used can be made out of graphite material. High pressure on the other hand requires the design of special dies and equipment that can withstand such conditions. Furthermore, low pressure use will help realization of larger composite bodies and complex shapes.

The aim of this research is to produce an ultra-hard diamond-SiC composite under low pressure conditions. To study the main parameters that control the formation of said composite material and developing a model for its synthesis. The final product should have in it no graphite phase and as little of free silicon as possible, preferably less than 1 vol% because this is a soft phase and will compromise the overall hardness of the material and its physical properties. A little silicon in the final product presents some advantage on one hand because during cooling it expands and introduces some compressive stress in the product which helps rid of any residual pores that may still exist within the structure.

Firstly a reaction-sintering route was explored in making the composite material. Additionally the infiltration route was experimented with. A eutectic Si-alloy was employed (where infiltration route is taken) to determine if lowering the infiltration temperature will help achieve full infiltration before product choking occurs. The temperature was raised after infiltration to drive the reaction to more product formation. Hardness, fracture toughness and application ability of dense materials obtained were investigated.
REFERENCE:


22. M. Kokkengada et al, Low viscosity resin infiltration technique used in rapid tooling, *International Conference of Flexible automation and Intelligent Manufacturing*, UMD, Maryland, June 2000


