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

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CHAPTER TWO

2.1 The Materials

Diamond is an allotrope of carbon where the carbon atoms are arranged in a cubic crystal lattice. It is the hardest known naturally-occurring mineral with a hardness of 10 on Moh's scale of mineral hardness [1]. Presently, only aggregated diamond nanorods, a material created using ultrahard fullerite (C_{60}) is confirmed to be harder, although other substances such as cubic boron nitride, rhenium diboride and ultrahard fullerite itself, are comparable [1]. Its hardness and high dispersion of light makes it useful for jewelry and industrial applications such as cutting and grinding tools, wear parts and drilling materials. The hardness of diamond is considered to be a product of the crystal structure and the strength of the sp^3 C-C bond.

Diamond is specifically renowned as a material with superlative physical properties. Diamonds makes excellent abrasives and hold a polish extremely well and retain their lustre [1]. The other exceptional physical characteristics of diamond include its high refractive index and extremely high thermal conductivity. Above 1700 °C, at atmospheric pressure, diamond converts to graphite [1, 15]. Naturally occurring diamonds have a density ranging from 3.15 to 3.53 g/cm³, with very pure diamond typically extremely close to 3.52 g/cm³. Below is a table showing the properties of diamond (Table 2.1)

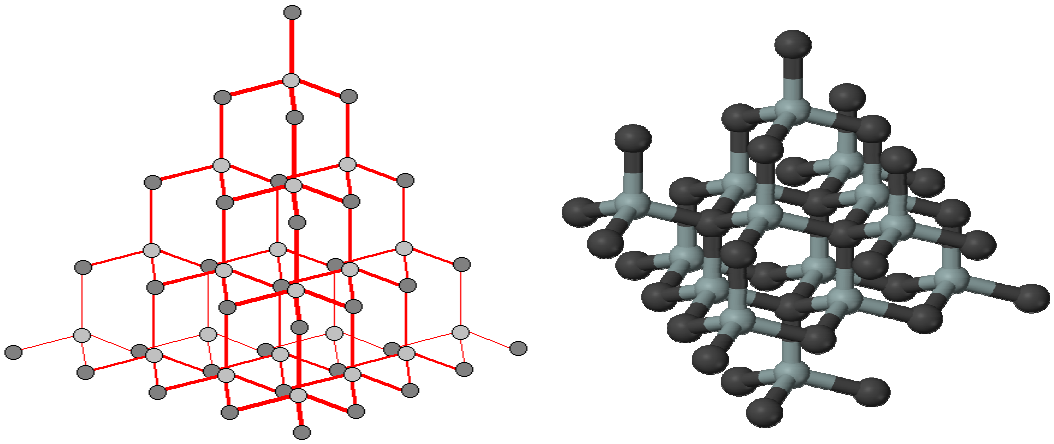
Table 2.1: *Properties of diamond [18].*

Property	Value	Units
Hardness	10,000	kg/mm^2
Strength, tensile	>1.2	GPa
Strength, compressive	>110	GPa
Sound velocity	18,000	m/s
Density	3.52	g/cm^3
Young's modulus	1.22	GPa
Poisson's ratio	0.2	Dimensionless
Thermal expansion coefficient	0.0000011	/K
Thermal conductivity	20.0	W/cm-K
Thermal shock parameter	30,000,000	W/m
Debye temperature	2,200	K
Optical index of refraction (at 591 nm)	2.41	Dimensionless
Optical transmissivity (from nm to far IR)	225	Dimensionless
Loss tangent at 40 Hz	0.0006	Dimensionless
Dielectric constant	5.7	Dimensionless
Dielectric strength	10,000,000	V/cm
Electron mobility	2,200	$cm^2/V\text{-}s$
Hole mobility	1,600	$cm^2/V\text{-}s$
Electron saturated velocity	27,000,000	cm/s
Hole saturated velocity	10,000,000	cm/s
Work function	small and negative	On [111] surface
Bandgap	5.45	eV
Resistivity	10^{13} - 10^{16}	Ohm-cm

Because of its hardness, it becomes very difficult to make diamond tools of various shapes and sizes because large diamonds can not be produced purely from cutting and shaping diamond. This problem led to the development of diamond composite materials which consist of small diamond grains either intergrown into each other or held together

in a matrix by a binder phase material. The introduction of the binder phase or a liquid sintering aid to consolidate the diamond crystals, which on their own are brittle, improves the shape versatility as well as the fracture toughness of the resulting composites [2].

Although the use of liquid phase sintering aids helps make a very useful class of ultrahard materials, the remains of the sintering aid promote graphitization of diamond at temperatures as low as 700°C [3]. Silicon carbide was however found to be an exceptionally good diamond binder phase. Silicon carbide does not react with diamond and is highly stable at high temperatures thus enabling diamond-SiC composites to be applicable at higher temperatures. Due to the individual thermal conducting nature of both diamond and silicon carbide, the diamond-SiC composites in turn exhibit a high thermal conductivity hence they find their use mainly in thermal applications such as heat conducting cutting tools and heat sinks. The silicon is introduced into the diamond preforms by either reaction sintering silicon powder and diamond powder or infiltrating a diamond preform with molten silicon. The silicon carbide matrix adheres very strongly to the diamond particles thus resulting in a very strongly bonded composite. This is due to SiC exhibiting the same cubic crystal structure (Fig 2.1) as diamond and therefore they form a coherent matrix (interlocking) together where the silicon carbide is formed from the diamond in-situ [4]. The lattice parameters of diamond and SiC are comparable, with diamond having a lattice parameter that is about 82% to that of SiC. The lattice parameters of diamond and SiC are 3.57Å and 4.36Å at 300K.



a) Diamond structure *b) Silicon carbide structure*

Fig 2.1: *Structural similarities between diamond and silicon carbide*

Diamond-silicon carbide composites can be made through infiltration of diamond powder by silicon at high and normal pressures, high pressure sintering of diamond/SiC powder mixtures and by the synthesis of diamond/β-SiC composite films by microwave plasma assisted chemical vapour deposition [5]. One major advantage to the reactive infiltration technique is the avoidance of porosity defects. Residual silicon of relatively low melting point (1410 ℃) is detrimental to high-temperature application, so it has to be minimal in the final product [6].

Developments in the manufacturing process of diamond-silicon carbide composites, such as addition of nanosize diamonds and silicon and structure engineering of grain boundaries, renewed interest in the investigation of the process and the mechanical properties of the composite product [7, 8]. Several different techniques have been used for diamond-SiC composites manufacturing. Among them, the most important was the high-pressure and high-temperature reactive infiltration technique. However the use of high pressures requires using special presses and dies and these severely increases the

production costs and also give rise to limitations in the possible sizes and shapes of the products made.

Reaction sintering is a method whereby objects are made by reacting two components in a mix in order to produce a third, ceramic phase. The high temperature needed to initiate the reaction is sometimes further boosted by the heat generated from the enthalpy of the reaction taking place. This high temperature further serves to sinter the particles of the new phase generated into a generally dense ceramic body. However, for the reaction sintering route, voids seem to be a problem if the reaction proceeds under low pressure conditions, due to volume reduction occurring during the reaction of carbon with silicon to form silicon carbide [9]. This phenomenon becomes increasingly more pronounced with decreasing size of the diamond crystals.

When the reaction-sintering route is used, under high-pressure high-temperature conditions (5-8 GPa and 1400^{o}C-2000^{o}C), it is claimed that nano-sized SiC is formed [10]. The overall material has a better fracture toughness than that obtained via the infiltration technique. The better fracture toughness is due to the nanostructure of the SiC compared to the micron size SiC that forms in the infiltrated samples (Fig 2.2) [10]. The hardness values of the reaction sintered products are however less than those of the infiltration-produced counterparts, which was attributed to the smaller residual strain of the SiC in infiltrated products.

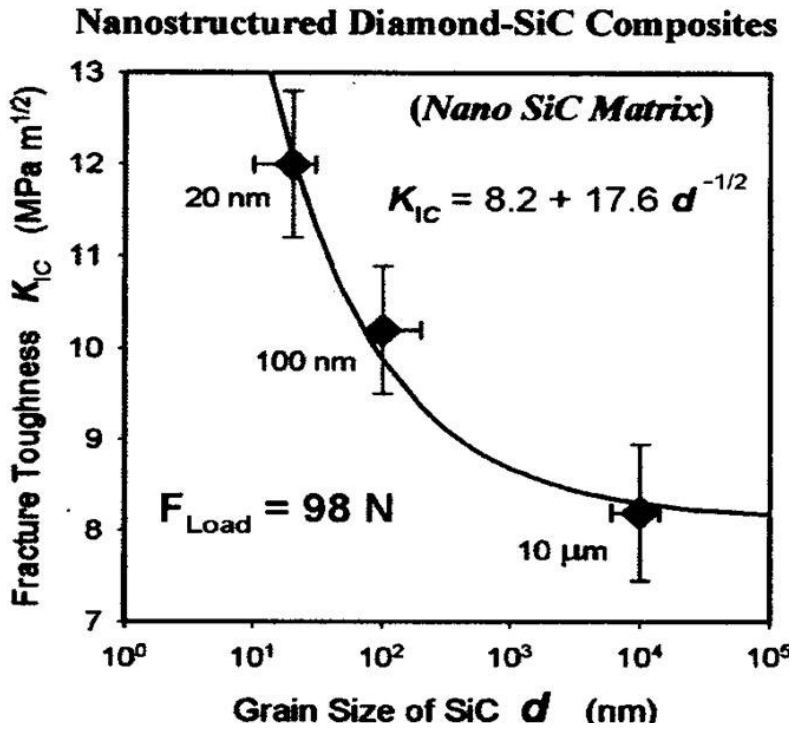


Fig. 2.2: *The relationship between the fracture toughness of the diamond-SiC composite and the grain size of its matrix. The diamonds indicate the measured fracture toughness values for the corresponding SiC grain sizes* [11].

Depending on the ultimate use of the material, either the fracture toughness or the hardness can be maximized by properly choosing the synthesis route. Most research on the production of diamond composites was done under the so-called diamond stable conditions since diamond graphitizes at elevated temperatures and low pressure. Also, since the melting point of silicon decreases with an increase in pressure, an increase in pressure allows for infiltration at lower temperatures thus diamond will not graphitize. The advantage of using low pressure is that composites of complex shapes and large sizes can be manufactured. However, it has been proved that it is possible to produce diamond-SiC composites successfully under the diamond unstable conditions, without the diamond graphitizing. Gordeev and Zhukov [12] managed to produce a fully dense material by

pressure-less infiltration. They used partially graphitized diamond green compacts. M. Shimono and S. Kume [13] produced diamond-SiC composites under temperatures of 1300^0C-1500^0C using the HIP method. The micrographs of the polished surfaces of the product revealed that it consisted primarily of two phases with few pores. XRD showed the coexistence of diamond and SiC. No trace of conversion reaction from diamond to graphite was seen, although the sample was treated under conditions in which diamond was thermodynamically unstable.

2.2 Infiltration Theory

Infiltration (also known as sinter casting) is a process whereby a molten phase is wicked into the open pores of a previously sintered porous structure [14]. The liquid is added from an external source. For infiltration to occur, the structure to be infiltrated should have pores which are open and interconnected. The preform to be infiltrated should have at least 10% porosity [14]. Infiltration offers the advantages of sintering at lower temperatures, shorter processing time, possibility of fully dense products, elimination of porosity with minimal dimensional change and near net-shaping without necessarily requiring application of an external pressure. It can also be successfully performed at low pressures giving a dense product. Below is a schematic illustration of the infiltration sequence (Fig 2.3).

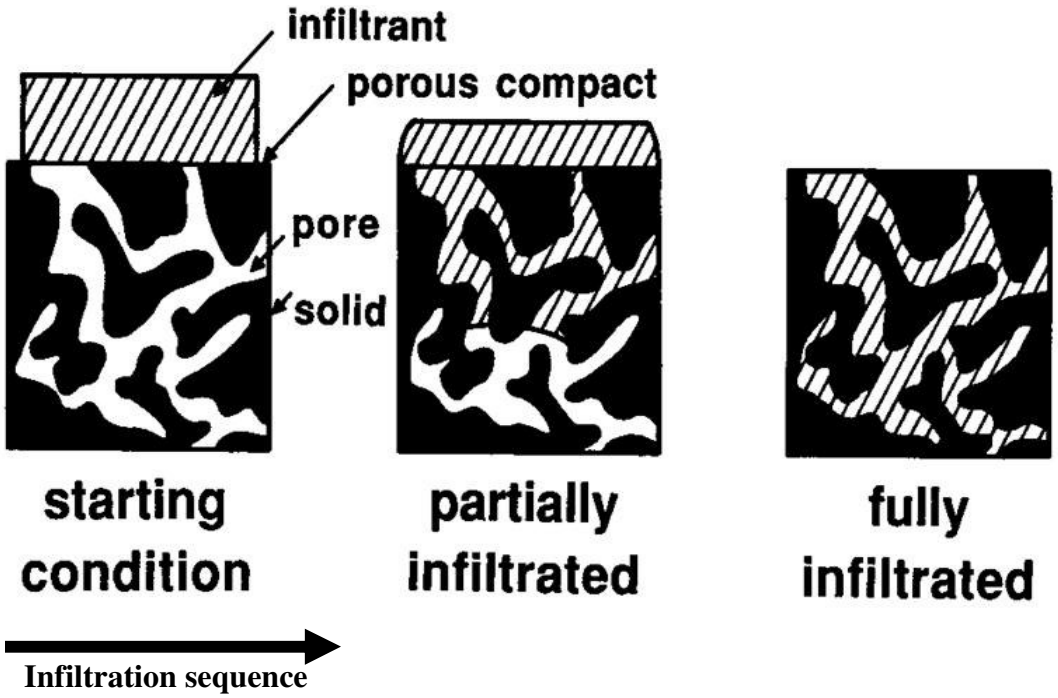


Fig 2.3: *Schematic infiltration sintering, where the pore space in a powder or sintered porous structure is filled with molten phase by cycling to a temperature between the melting points between the two materials* [14].

Infiltration can occur in two different ways, namely reactive infiltration and non-reactive infiltration. For a reactive infiltration system, there is interaction (reaction) between the melt (infiltrant) and the preform whereas for the non-reactive infiltration system, there is no interaction (reaction) between the melt and the preform. The former system mainly depends on the wetting behaviour and the reaction between the melt and the preform whereas the latter system depends on the wetting behaviour of the melt and the preform only. The infiltration process is sensitive to surface contamination therefore it requires clean surfaces for wetting.

2.2.1 Non-reactive infiltration

For the non-reactive infiltration system, the wetting behaviour of the liquid and the preform material plays a major role. The wicking of the melt only occurs if the liquid wets the solid phase. The wetting and spreading of a liquid on a solid surface depend on short range molecular forces that can be modified by a monolayer coating. Wetting may cause compressive forces between particles and liquid migration.

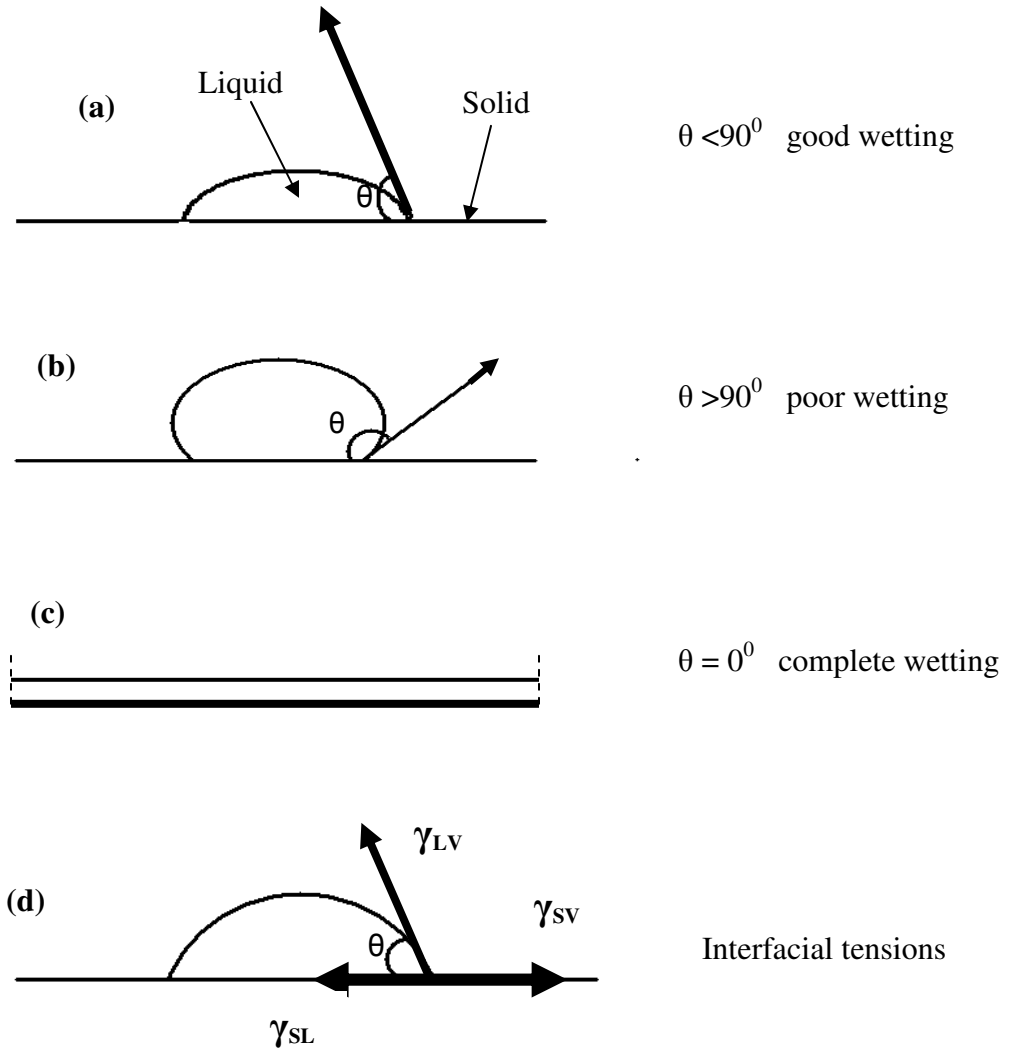


Fig 2.4: *Wetting behaviour between a liquid and a solid showing* ***a)*** *good wetting* ***b)*** *poor wetting* ***c)*** *complete wetting and* ***d)*** *the balance between the interfacial tensions for a liquid with contact angle* θ [16].

A system with $\theta<90^0$ is considered as wetting and a system with $90^0<\theta<180^0$ is considered as non-wetting.

The wetting angle of the interfacial tensions at the liquid-vapour-solid juncture is described by the Young equation ($\theta>0$).

$$Cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (2.1)\ [16]$$

Where $\boldsymbol{\gamma_{SV}}$, $\boldsymbol{\gamma_{SL}}$ and $\boldsymbol{\gamma_{LV}}$ are the effective interfacial tensions as indicated in Fig. 2.4 (d).

Assuming cylindrical pore channels, the height of infiltration (height risen by the fluid in the preform), that can be obtained from the capillary force is:

From:

$$\Delta P = \frac{2\gamma_{LV}\cos\theta}{R_c} = \rho g \Delta H \qquad (2.2)$$

Thus $$\Delta H = \frac{\Delta P}{\rho g} = \frac{2\gamma_{LV}\cos\theta}{R_c \rho g} \qquad (2.3)\ [16]$$

Where: ΔH = height risen by the liquid

ΔP = internal pressure

ρ = density of the liquid

g = acceleration due to gravity

R_c = pore radius

γ_{LV} = surface tension

θ = contact (wetting) angle

It can be deduced from equation 2.3 that fine pores give rise to a higher liquid rise (i.e. provide a greater suction) than larger pores.

Capillary pressure provides the driving force for infiltration and good wetting on the surfaces by the liquid is a key requirement. The kinetics of infiltration is complex [17]. However, if the pore structure of the preform is simplified as a set of parallel cylinders, the kinetics can be determined from Poiseuille's equation of viscous flow through a tube. The average laminar flow velocity (υ) of a column of liquid in a horizontal cylindrical capillary is therefore given by the Poiseuille equation.

$$\upsilon = \frac{\Delta P R_c^2}{8\eta L} \qquad (2.4)\ [17]$$

Combining equations 2.2 and 2.4, thus,

$$\upsilon = \frac{\gamma_{LV} \cos\theta R_c}{4\eta L} \qquad (2.5)\ [17]$$

Where η = viscosity of the liquid

L = length filled by the liquid.

From equation 2.5, it can be seen that the rate of penetration of the liquid into a preform, will be greater for a liquid of lower viscosity and higher surface tension and for pores of larger radius [17].

If time is taken into consideration during infiltration, the depth of infiltration varies with the square root of time. The height infiltrated in time *t* is then found to be:

$$h^2 = \left(\frac{r\gamma \cos\theta}{2\eta} \right) t \qquad (2.6)\ [19]$$

Where, h = height of infiltration

r = radius of the tube

γ = surface tension of the liquid

θ = contact (wetting) angle

t = time taken for infiltration

η = viscosity of the fluid

Equation 2.6 shows that the rate of infiltration is proportional to the pore size. Since the pore size increases with the particle size, preforms made with larger particles are more readily infiltrated [19]. Theoretically, it is possible to calculate the green density of the preform required to produce a fully dense composite, but in practice it is necessary to leave additional porosity to allow the infiltrating liquid to move freely.

In a non-wetting system, infiltration does not readily occur, as opposed to the wetting system. In-fact a liquid that is non-wetting tends to force particles apart. For such a

system, for infiltration to take place, an external pressure has to be applied. This pressure should be greater than the maximum capillary resistance of the preform to the penetration of the liquid melt into the largest interfaces [19]. Darcy's law states that:

$$h^2 = \frac{2kt}{\mu(1 - V_p)}\Delta P \qquad (2.7)\ [21]$$

Where, h = infiltration height

t = infiltration time

k = intrinsic permeability

V_p = particle volume fraction of packed sample

μ = viscosity of liquid melt

ΔP = pressure drop in the liquid

When a plot of h^2 against pressure is done, we get a straight line and this also shows the threshold pressure (P_o) that is needed to kick-start infiltration [21].

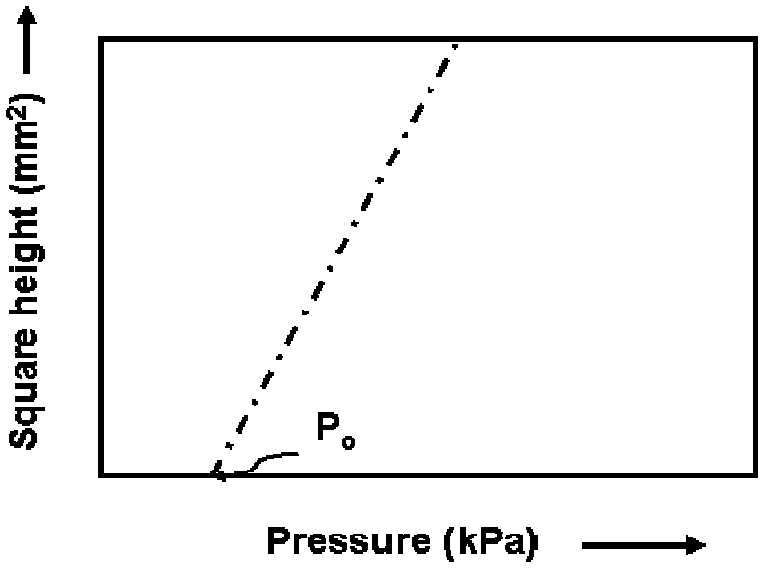


Fig 2.5: *An illustration of Darcy's plot of infiltration height vs. pressure* [27].

2.2.2 Reactive Infiltration

For a reactive infiltration system, the wetting behaviour and the rate of reaction of the system plays a major role. There are many factors that influence these parameters. Good wetting is an important factor during reactive infiltration. A liquid possessing a low contact angle readily wets the solid thus allowing easier wicking of the liquid into the pores. Both carbon and SiC show good equilibrium wetting with liquid silicon.

Another important factor in such systems is the pore size distribution and porosity. For infiltration to occur, the preform should have at least 10% porosity and pores which are open and interconnected [14]. There is volume expansion of the solid phase during the reaction in the diamond-SiC system, so this means that there exist an optimal pore diameter that should allow full infiltration and at the same time accommodating this volume expansion. In the diamond-SiC system, too large pores are undesirable because

there will be a high probability of ending up with free silicon in the final product. This occurs because the Si, which remains after formation of the dense SiC layer around the diamond, reacts only very slowly because this reaction is controlled by the diffusion through the SiC layer. Free silicon is undesirable because it limits the application of the product at high temperatures and it impairs the mechanical properties.

For reactive infiltration to occur, temperature also plays a major role. Infiltration is carried out at temperatures higher than the melting point of the infiltrant but less than the softening or deformation temperature of the preform. Higher temperatures greater than the melting point of the infiltrant also have an advantage of reducing the melt viscosity thereby allowing easier wicking of the melt into the porous preform. The temperature has to be strictly controlled though, because in some systems like the diamond-SiC one, temperatures should not go above 1600^0C because diamond graphitizes at this temperature under low pressures. This means there is a need to establish the refractoriness of the preform material so that maximum temperatures can be determined which will allow the melt viscosity to be reduced without compromising the preform material.

In most cases, the reaction and infiltration occur simultaneously. Also sometimes, as in the diamond-silicon system, the rate of product formation is very fast and this results in blocking of the pore channels thus making further infiltration of the preform very difficult. So in order to maintain an interconnected porosity, ways should be found that can retard the rate of reaction (product formation) so that this phenomenon is curbed. If

the system is non-wetting, an external pressure is required to force the liquid into the pores. Even if the system is wetting, the external pressure can also be used to accelerate the rate of infiltration and also help the melt to reach the much smaller pores.

2.3 Carbon-Silicon Interactions

The reaction between carbon and silicon to form silicon carbide is mainly thought to be a diffusion process though existing literature presents conflicting interpretations of the mechanism of the reaction. The assessed equilibrium phase diagram of the Si-C system is presented in Fig. 2.6. The diagram indicates a peritectic transformation at 2 545 ± 40 ^{0}C involving SiC and a liquid of 27 atom % C and a eutectic transformation at 1 404 ± 5 ^{0}C, with a eutectic composition of 0.75 ± 0.5 atom % C. Both transformations involve the intermediate compound SiC.

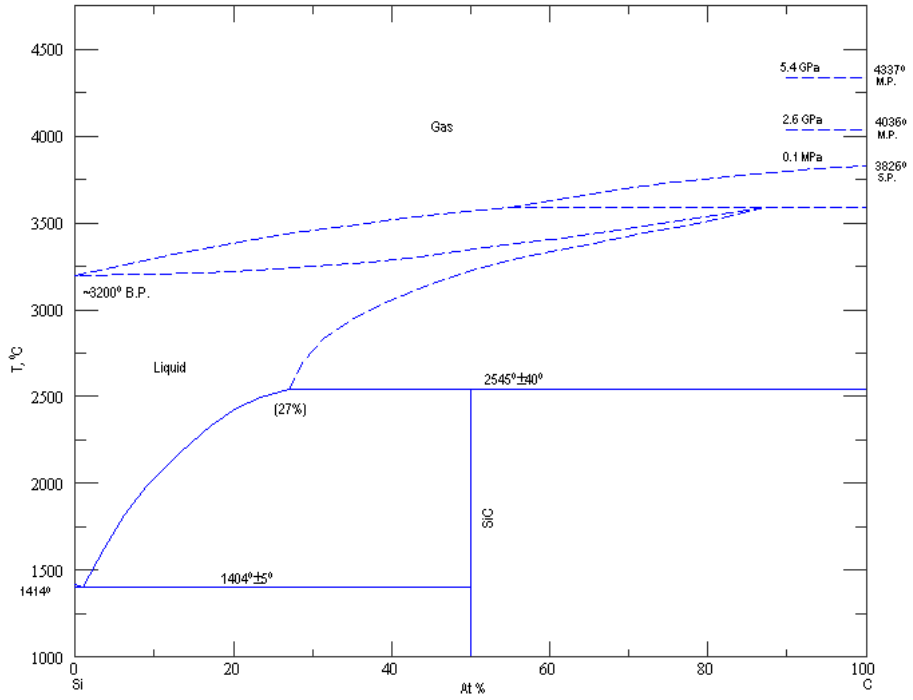


***Fig. 2.6**: Equilibrium phase diagram of the carbon-silicon system [22].*

Researchers, Olesinski and Abbaschian [22], studied the thermodynamics of the Si-C system to determine the stability of various phases of the Si-C system. They concluded that silicon carbide is a thermodynamically stable compound, with the cubic form (βSiC) more stable than the hexagonal form (αSiC) at any temperature below the peritectic point. The heat of formation from the elements is given by: ΔH^0_{298} = - (69 - 73) kJ/mol, which means a distinctive exothermal chemical reaction [23].

Studies on the kinetics and the reaction mechanism of the SiC formation from different precursors have been reported and several theories have been put forward. There is a general agreement that the rate controlling step of the reaction is the diffusion of carbon

atoms through the newly formed SiC layer with activation energies of 100–400 kJ/mol [24]. It has been observed that reaction proceeds faster for diamond crystals of smaller sizes and when the temperature is increased. It has also been generally accepted that the reaction between diamond and liquid silicon starts on the surface of the diamond crystals, near the surface defects [24, 25]. These surface defects that promote the reaction between diamond and melted silicon are of microscopic level and consist of growth steps, surface dislocations and places of increased roughness [24].

C. Pantea *et al* [24] concluded that the reaction between diamond and silicon starts at the defects on the diamond crystals. The SiC formed then grows laterally and vertically thereby forming SiC islands. These islands overlap and quickly cover the surfaces of diamond crystals. When the entire surface has been covered, the diffusion mechanism of the reacting species controls further growth.

K. Mlungwane *et al* [26, 27] also studied the interaction of diamond and silicon. They found out that after the onset of the reaction, a SiC layer of 5-10μm thickness is formed very quickly on the surface of the diamond particles. The thickness of the layer is controlled by the density of the nuclei formed. If the amount of nuclei is large, the thickness of the layer formed would be lower thus giving rise to a possible higher infiltration depth.

Other suggestions pointed that the vacancy mechanism is responsible for the diffusion of silicon and carbon through βSiC [28]. Carbon is the faster diffusing component in the lattice of βSiC due to its smaller atomic size. The lowest energy migration route is

believed to be the direct jump to the nearest Si vacancy without the occupation of an intermediate vacant octahedral position. The diffusion constants of carbon and silicon in βSiC are given in Fig. 2.7.

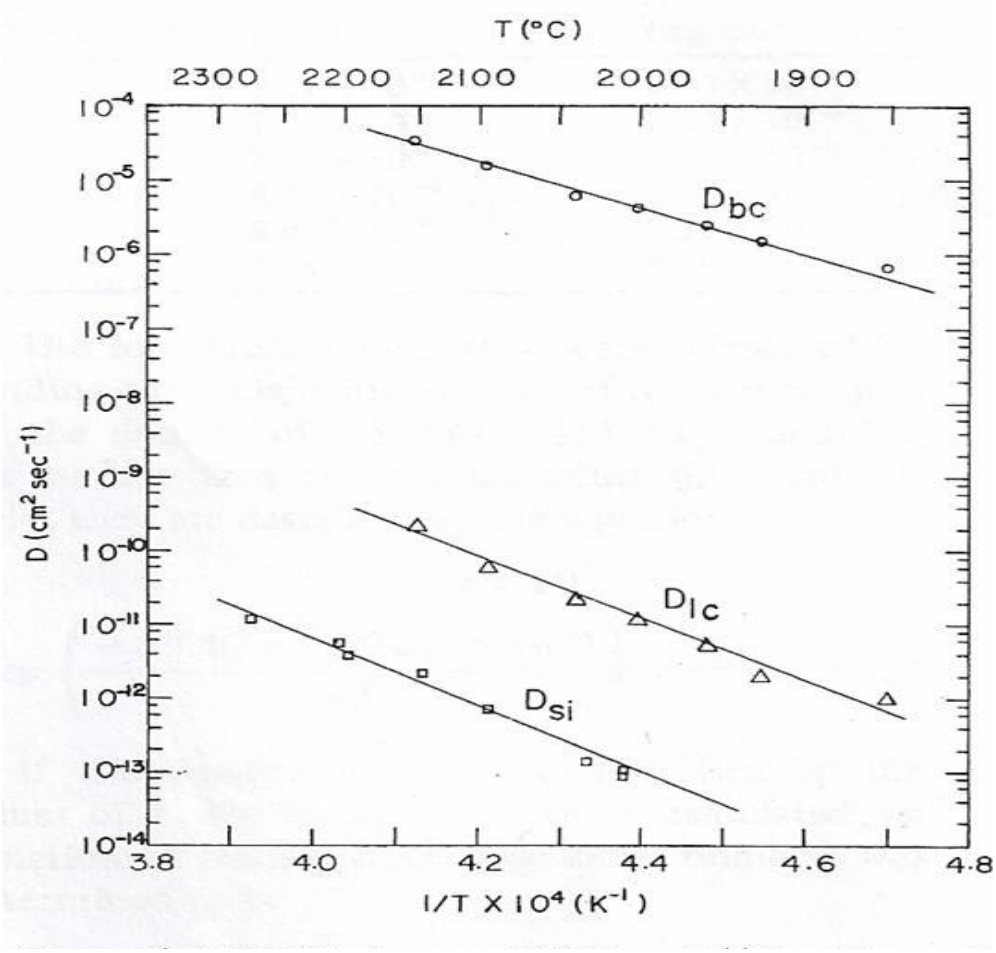


Fig 2.7: *Self-diffusion coefficients of ^{14}C lattice diffusion (D_{lc}), ^{14}C grain-boundary diffusion (D_{bc}) and ^{30}Si lattice diffusion (D_{si}), in βSiC as a function of 1/T [28].*

Fitzer and Gadow [23] investigated the reactivity of different carbons with liquid silicon. They found out that the microstructure and porosity of the original carbon determines how the heterogeneous chemical reaction between carbon and liquid silicon takes place. The reaction mechanism involves three stages: a silicon mass transfer by volume diffusion caused by capillary effect, the complete wetting of molten silicon on pure

carbon surfaces and the grain boundary and bulk diffusion of silicon through the primarily formed SiC layer. The structure of the SiC layer on the inner and outer surface of the sample determines the effective diffusion coefficient. This further supports the theories that the reaction between carbon and silicon is mainly a diffusion process. However, Hase and Suzuki [31] found no continuous product layer between carbon particles and silicon. They suggested that the reaction product quickly spalled owing to the volume misfit between SiC and carbon leading to an interface-limited reaction directly between silicon and carbon.

Sawyer and Page [29] and Ness and Page [30] also proposed a different reaction mechanism. They proposed that the reaction mechanism is mainly a solution re-precipitation mechanism. The SiC is precipitated from a supersaturated solution of graphite in liquid silicon on to local nucleation sites. The rate of carbon dissolution is accelerated by the heat evolved in the reaction and this allows the reaction to go to completion. The highest dissolution of carbon in silicon is believed to be at the reaction front since the reaction is highly exothermic and the supersaturation is believed to exist in the cooler regions away from the reaction front [32]. The newly formed SiC grows as the β-polytype and nucleates either on the existing grits or less frequently, on the graphite or even homogenously [30]. The finely dispersed βSiC forms during the local cooling down of the liquid silicon immediately behind the reaction front and thus never experiences sufficient thermal activation to transform to αSiC. Zhou and Singh [32] supported this solution-precipitation mechanism. They found SiC precipitates in the silicon phase and this was assumed that

carbon had dissolved in the liquid phase and got carried away into the silicon phase and finally precipitated as SiC during cooling.

The kinetics of the reaction between carbon and silicon has also been studied. Zhou and Singh [32] studied the reaction kinetics of glass carbon and a pure silicon melt. In their study, they found out that most of the SiC was formed during the early stage of the reaction and the growth rate of the SiC layer decreased in the latter stage of the reaction. A model which can explain the experimentally observed rate law was proposed, in which a negative space charge was assumed to exist in the growing SiC layer. The diffusion of the carbon-ion vacancy through this layer under an electric field is proposed as the rate-limiting step for the growth of the SiC layer [32]. A critical analysis of the data of Zhou and Singh [32] would suggest that there is a change in the mechanism after the layer has formed. Assuming such change in the reaction mechanism, there is no necessity for a forth power rate law to describe the data. The time dependence of the growth of the SiC film itself is difficult to determine due to the low growth rate and the relative low time of the experiments.

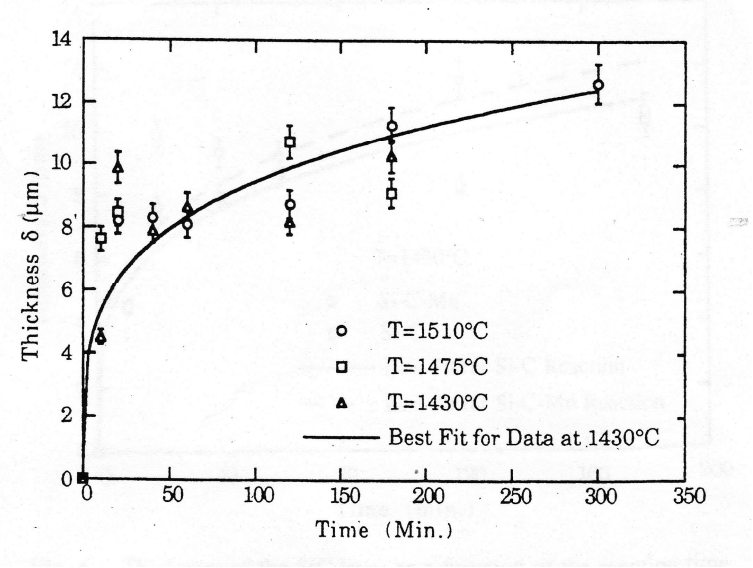


Fig. 2.8: *Thickness of the SiC layer as a function of the reaction time for Si-C at 1430 ^{0}C, 1475 ^{0}C and 1510 ^{0}C [32].*

From Fig. 2.8, it can be observed that an increase in the reaction time gave rise to an increase in the SiC thickness layer. There is a sharp increase in the SiC thickness at the initial stages of the reaction and then it slows down as the reaction progresses.

From the work done by K. Mlungwane [27], the results found indicated that the reaction rate of diamond and glassy carbon are very similar and that the reaction is likely to be controlled by some transport processes. It was concluded that during wetting of diamond by Si, the SiC nucleates and grows along the surface. Between these nuclei, at the grain boundaries of diamond, the carbon dissolves into silicon and then it is transported through the liquid to the growing crystals. The rate of nucleation and the growth rate seem to increase with temperature hence the interface becomes less rough during reaction at higher temperatures. After the coalescing of the crystals, the overall growth rate

decreases and further growth takes place by the diffusion of Si and C through the grain boundaries [27]. The diffusion process is very slow hence the fast reaction at the beginning, before a dense layer forms. The reaction mechanism changes from transport through liquid to transport along grain boundary. This process is schematically illustrated in Fig 2.9. The thickness of SiC layer formed from the reaction of Si with diamond is also shown in Fig 2.10.

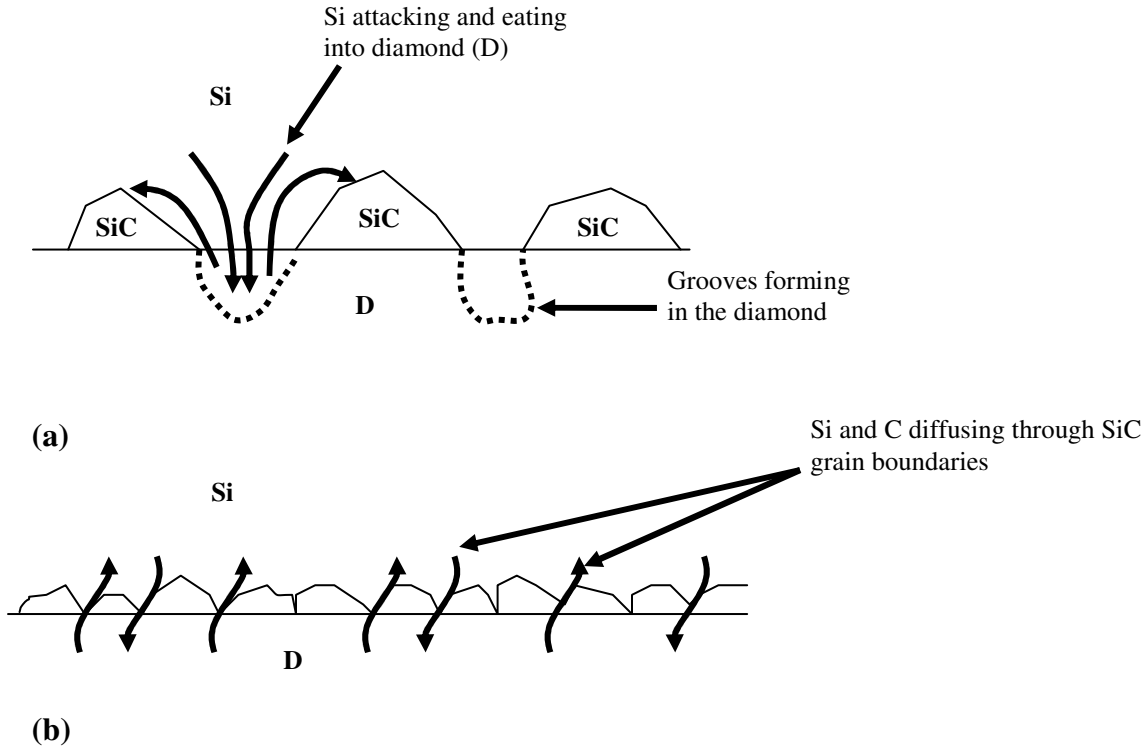


Fig 2.9: *A schematic illustration showing the formation and growth of SiC* ***a)*** *in the starting period of layer formation and* ***b)*** *after the layer is formed* [27].

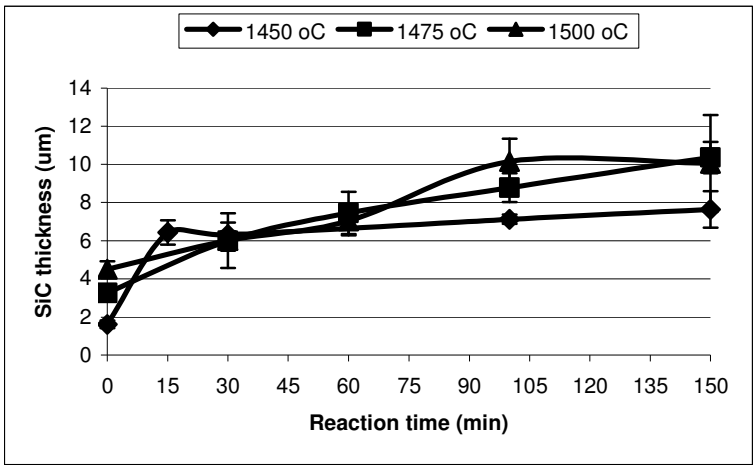


***Fig 2.10**: The thickness of SiC layer formed from the reaction of Si with diamond [27].*

C. Pantea *et al* [24] also studied the kinetics of the reaction between diamond and silicon under high pressure and high temperature. They also found that the formation of SiC takes place rapidly at the start of the reaction and then it slows down as the reaction proceeded. The results are plotted in Fig. 2.11.

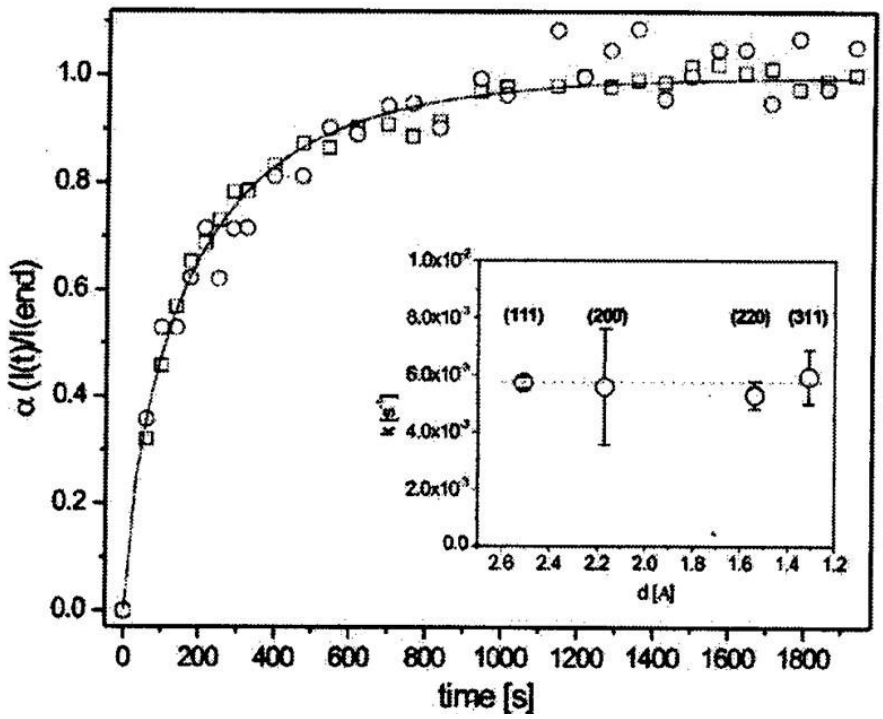


Fig 2.11: *Plot of the degree of reaction of diamond and silicon, α, vs. time. Solid line represents the best fit of the Avrami-Erofeev equation to exponential data for the (111) reflection. The insert shows error bars in reaction rate, k, determination for the different reflections of SiC* [24].

2.4 Coating of diamond

There has been an increase in the actual and potential uses of diamond and carbon/carbon composites especially in high temperature applications when they may be exposed to an oxidizing atmosphere or be in contact with metal alloys. This results in detrimental effects on carbon surfaces or carbon/metal interfaces and deterioration of mechanical properties of parts made from diamond or carbon/carbon composites. In order to prevent these detrimental interactions, the surface of the diamond should be modified by coating with a protective ceramic layer [33]. Diamond can also be coated with different protective

layers in order to improve its surface properties. Diamond grains coated with nickel or copper are used for resin bonded diamond wheels for their high bonding strength [34] but these coating metals flow and cause loading during grinding and the coated grains are not suitable for vitrified bonded diamond wheels.

The most common ceramic coatings on diamond are TiC and SiC because they adhere tightly to diamond surfaces. Titanium carbide is a well known coating material used in industrial applications due to its good wear resistance, corrosion resistance and high hardness [33, 36]. TiC also has a high melting temperature, good thermal shock resistance and good chemical and physical sputtering resistance under bombardment by highly energetic particles [33, 37]. On the other hand, SiC is an excellent candidate for high temperature structural applications because of its exceptional range of mechanical and thermal properties [35]. The ceramic coatings can be applied via a number of processes namely chemical vapour deposition (CVD), physical vapour deposition (PVD) and powder immersion reaction assisted coating (PIRAC), among others [33]. Depending on the deposition method and processing conditions used, the coating properties vary significantly. The disadvantage of CVD and PVD processes is a weak adhesion between the substrate and the coating, which can result in the coating peeling off. PIRAC has been found to be a low cost diffusional method surface modification that allows fabrication of coatings with strong adhesion to the substrate [33].

X. Yin *et al* [35] investigated the formation of TiC on graphite via PIRAC and they found out that in the presence of iodine, Ti atoms reach the surface of the coating mainly in the

form of gaseous titanium iodide by transport reaction. The reaction between carbon and Ti with the formation of TiC takes place on the coating surface. The rate of the reaction depends on the concentration of carbon and Ti on the surface. Tokura and Yoshikawa [34] also investigated ceramic coatings on diamond. They coated diamond with TiC using the CVD method in order to get a high bonding strength of diamond grains with other materials and to make them easier to handle in air. They found that if the TiC film wholly covers the diamond surface, it is possible to prevent diamond oxidation and it is easy to handle the diamond in air at high temperatures. Furthermore, they found that the adherence strength of TiC is higher on rough diamond surface than a smooth one.

For the purpose of this work, the diamond is going to be coated with TiC and SiC using the chemical vapour deposition method in order to delay the reaction between silicon and diamond thus curbing the detrimental effect of rapid pore closure during infiltration.

2.5 Project motivation

The possibility of driving the grain size of the diamond phase in SiC-Diamond composites down to 2μm for an infiltrated thickness of 2.5mm [26, 27] encouraged us to expect that there may be ways to further decrease the grain size of the phases present in the material, while at the same time increase the size of the parts that can be generated with such material. The production of 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 ambient pressure, as opposed to ultra-high pressure, the cost of production is enormously reduced.

The aim of this research is to produce an ultra-hard diamond-SiC composite with an average grain size of 2μm or less, and a thickness exceeding 2.5mm, preferably exceeding 5mm. This will be achieved by increasing the pore size of the preforms or by delaying the reaction time between diamond and silicon or by a combination of both. The pore size may be increased by varying the resin content in the preforms or varying the applied pressure (cold press) during the manufacture of the preforms. The reaction between diamond and silicon can be delayed by coating diamond with TiC or SiC before reacting with diamond. Hardness, fracture toughness and application ability of the composites obtained will be investigated.