

CHAPTER 7: Diamond-silicon carbide composite produced by infiltration with silicon

This chapter presents the results, discussion and conclusions drawn on the infiltration of diamond with pure silicon. Different temperature cycles were explored in order to optimise the infiltration conditions. The product of the infiltration was cross-sectioned and polished and characterized with SEM, XRD and optical microscope. Mechanical properties (hardness and wear behaviour) of the product were also determined.

7.1 Preform structure

After preparation of preforms (detailed in section chapter 3.3), the preforms' green density is determined using mass and volume of the preforms and the pore size distribution using mercury porosimeter after pyrolysis. The results are presented in figure 7.1 and table 7.1.

A trend is observed for both the D2 and D9 concerning pore size distribution in the green body as a function of resin content. As the resin content increases, the green density and the overall porosity decrease and the pore size increases. Higher resin content is expected to decrease the density because it is less dense than diamond. The overall porosity is also decreasing with increasing resin content. This could be attributed to the fact that the resin acts as a lubricant and in its presence the powder compacts more easily, hence when using the same compaction pressure the high resin content powder would compact into a less porous green compact than a low-resin one.

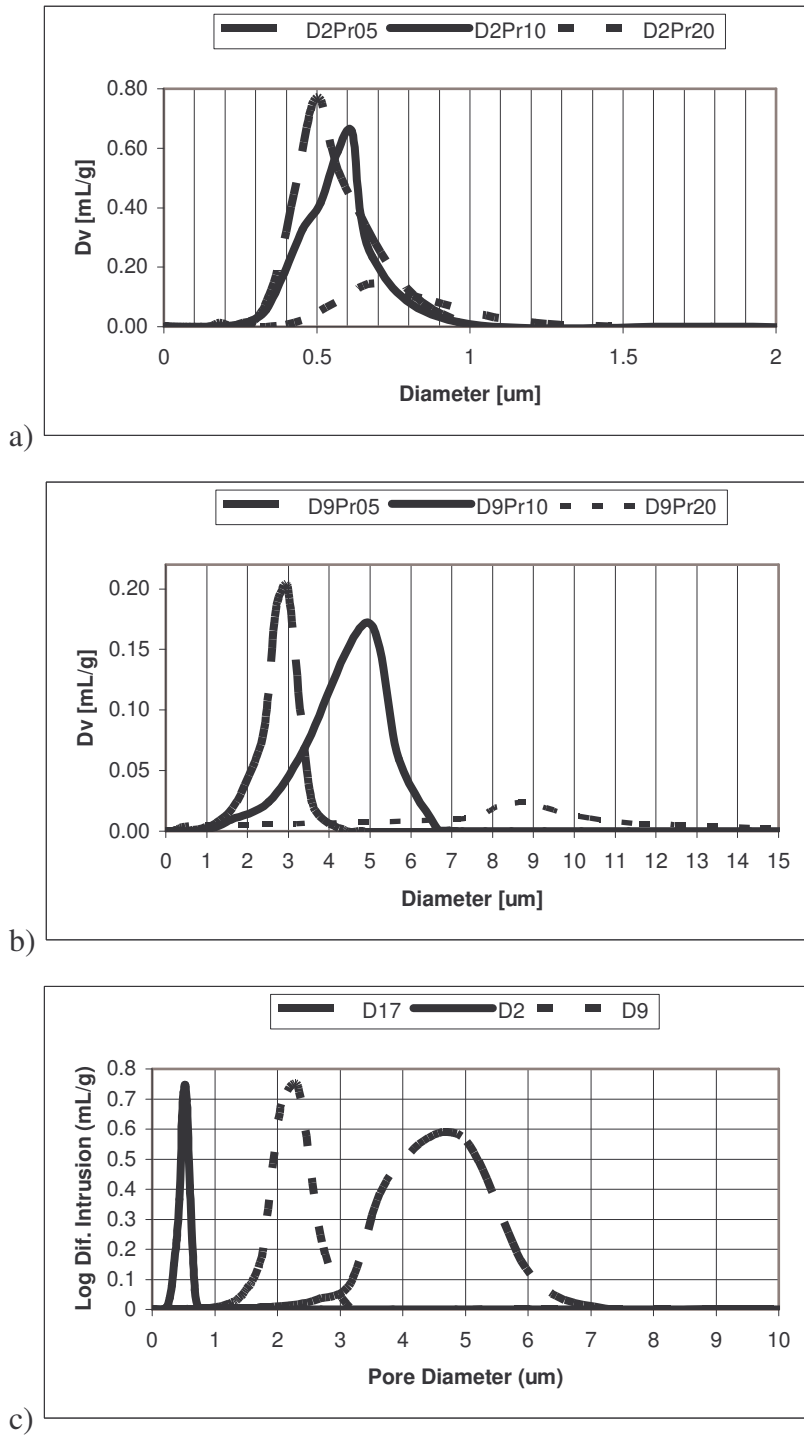


Fig. 7.1: The pore size distribution of preforms a) D2 with varying resin content, b) D9 with varying resin content, and c) 10 wt% resin in D2, 9 and 17.

When other parameters (table 7.1) are taken into account, green density, overall porosity and pore size are evaluated as a function of diamond grade, the trends seem to be resin-

content dependent. For the 5% resin-containing compacts, as the diamond particle size increases, the density also increases. However, as the resin content increases to 20%, a reverse relationship is observed, density decreases with large diamond particles. 5% resin helps to densify the preforms, and for small diamond grains more resin is necessary for pressing whereas for the large diamond grains no further increase in packing density takes place.

Increasing diamond particle size decreases the overall porosity in the green compacts but increases the mean pore diameter. This is caused by the fact that as the particle size gets bigger and so will the pores associated with them.

The infiltration procedure is described in chapter 3. All preforms were infiltrated at 1500°C, additionally some of them were infiltrated at 1450°C. Due to the small particle size of diamond and small interparticle distances, it is difficult to perform accurate image analysis on the fine diamond product (D2). A small over-covering or under-covering of the phases during the analysis results in a big error because the phases are so thinly dispersed in each other. The samples based on D2 were analysed at a magnification of 3000X to get a more accurate identification of the phases. The microstructures of the coarser grained materials (D9 and D17) were analysed using images with 1000X magnification.

RESULTS

Table 7.1: A summary of the infiltration results of the preforms containing different amounts of resin. (1) indicating full infiltration)

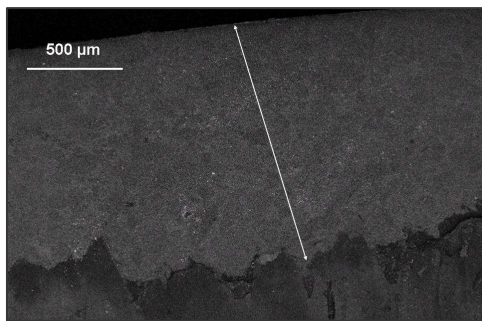
SAMPLE	D GRADE	RESIN (wt%)	WEIGHT LOSS (after pyrolysis) (%)	GREEN DENSITY (after pyrolysis) (g/cm³)	OPEN POROSITY (%)	MEAN PORE DIAMETER (µm)	FINAL DENSITY (g/cm³)	INFIL. HEIGHT (mm)		PHASE COMPOSITION		
								1500°C	1450°C		Vol %	
											1450 °C	1500 °C
D2R05	D2	5	1.86 ± 0.03	1.82	40	0.57	-	-	1.5	-	-	-
D2R10		10	4.11 ± 0.01	1.80	29	0.57	3.26 (1500°C)	-	2.5	D		36
										SiC		64
										Si		0
D2R20	20	8.74 ± 0.07	1.79	11	0.77	-	-	0.017				
D9R05	D9	5	2.00 ± 0.02	1.84	38	2.69	3.30 (1500°C)	-	2.3	D		46
SiC											51	
Si											3	
D9R10		10	4.10 ± 0.02	1.78	29	4.86	3.28 (1500°C) 3.29 (1450°C)	5 ¹⁾	5 ¹⁾	D	49	53
										SiC	51	47
										Si	0	0
D9R20	20	9.00 ± 0.03	1.71	15	8.79	-	-	0.097		-	-	
D17R05	D17	5	2.20 ± 0.15	1.97	25	5.75	3.32 (1500°C) 3.35 (1450°C)	5 ¹⁾	5 ¹⁾	D	45	52
SiC										52	40	
Si										3	8	

7.2 INFILTRATION OF DIAMOND

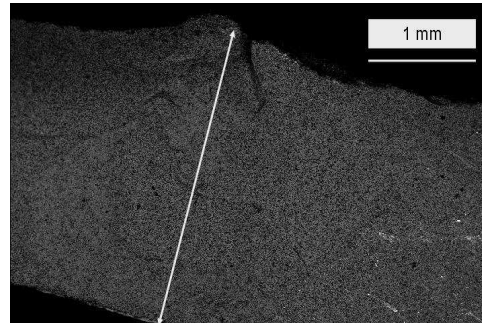
Infiltration of a carbon body by silicon, followed by reaction to form SiC is accompanied by volume expansion. This volume expansion on one hand is desirable because it can aid densification of the material by closing residual porosity as the product forms. The challenge however is to have big enough pores to accommodate the expansion as the product forms and still maintain open porosity until a desired infiltration height is obtained.

In this part of work different grades of diamond were infiltrated, coarse, medium and fine. A phenolic resin binder was used. The properties of the used preforms are summarised in Table 7.1.

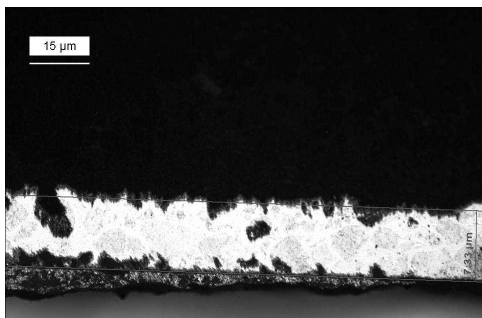
Below are micrographs showing the infiltration depths in the samples where non-full infiltration took place. Only the maximum infiltration heights obtained are shown.



a)



b)



c)

Fig. 7.2: Some cross-sections showing the maximum infiltration heights after infiltration at 1500 °C for 30 minutes of D2 diamond with a) 5 %, b) 10 %, and c) 20 % resin.

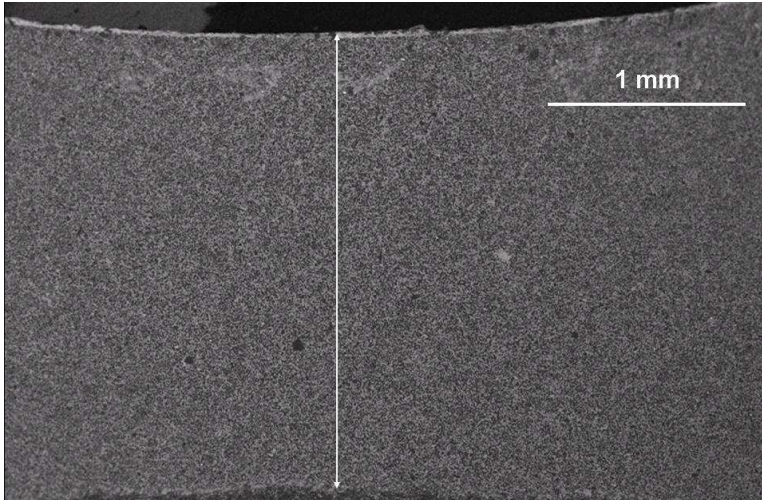


Fig. 7.3: A cross-section of D9 diamond with 5% resin showing the maximum infiltration height after infiltration at 1500 °C for 30 minutes.

Several infiltration experiments were performed on the coarse grained preforms under the same conditions, in all of them full infiltration was achieved indicating the results are reproducible. For the medium grade full infiltration could only be achieved with 10% resin content. The infiltration product is fully dense, no open porosity could be determined using the Archimedes principle, and no pores were evident either under the SEM. It seems that increasing the resin content in the medium grade diamond from 5 to 10% helped improve infiltration depth from 2.3 to 5mm (full infiltration). However, further increase of the resin content to 20% has a negative effect, it reduces the infiltration. The same trend is observed in the fine diamond grade also. Hence one can infer that there is an optimum resin content for the improvement of the infiltration depth.

It seems from the results above that there exists a combination of overall porosity and mean pore diameter from which full infiltration is achieved (see samples D9R10 and D17R05 in table 7.1). An overall porosity of 20 – 30% with a mean pore diameter between 4 – 6 μ m yields full infiltration. Sample D2R10 has a porosity of 29% that seems to have worked for sample D9R10, however its mean pore diameter is too low. A fine pore diameter would close much quicker due to the fast initial formation of SiC and stop any further infiltration by silicon. Too large a pore diameter (as in the case of non-preformed diamond) on the other hand has low capillary force and the resultant

infiltration height is less than it would be if the pore could be smaller. Therefore there exists an optimum pore diameter when low pressure infiltration is used.

When the diamond particle size is decreased, the reaction to form SiC seems to consume the 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.

Examples of typical SEM micrographs of the produced samples are shown in figure 7.4.

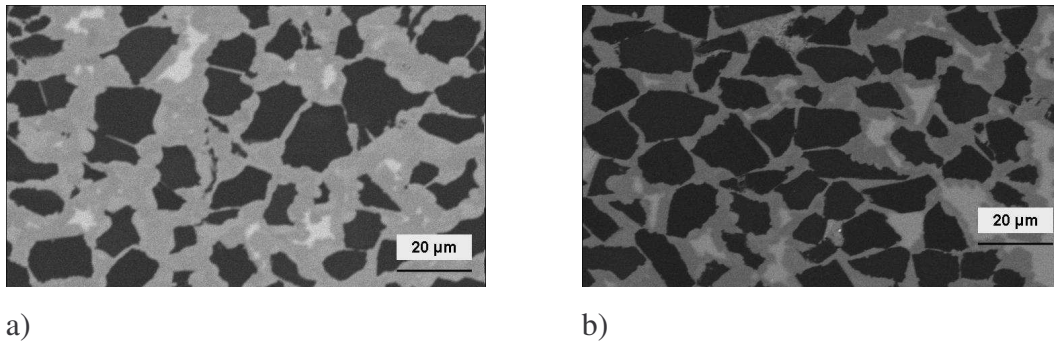


Fig. 7.4: Typical backscatter SEM micrographs of polished cross-sections of D17 diamond (5% resin) preforms infiltrated for 30 minutes at a) 1450 °C (vol% composition: Diamond = 45; SiC = 52; Si = 3) and b) 1500 °C (vol% composition: Diamond = 52; SiC = 40; Si = 8)

The presence of free silicon (white phase) is clearly visible in the case of samples produced from D17 diamond. The diamond (black phase) is homogeneously distributed. At the lower infiltration temperature there is less free silicon and more SiC (grey phase) than at the higher temperature.

No free silicon phase was detected in the D2 samples. The white phases seen are silicides formed by metals contamination (fig 7.5 – 7.6). EDS measurement on D9 shows that there is contamination by metal oxides.

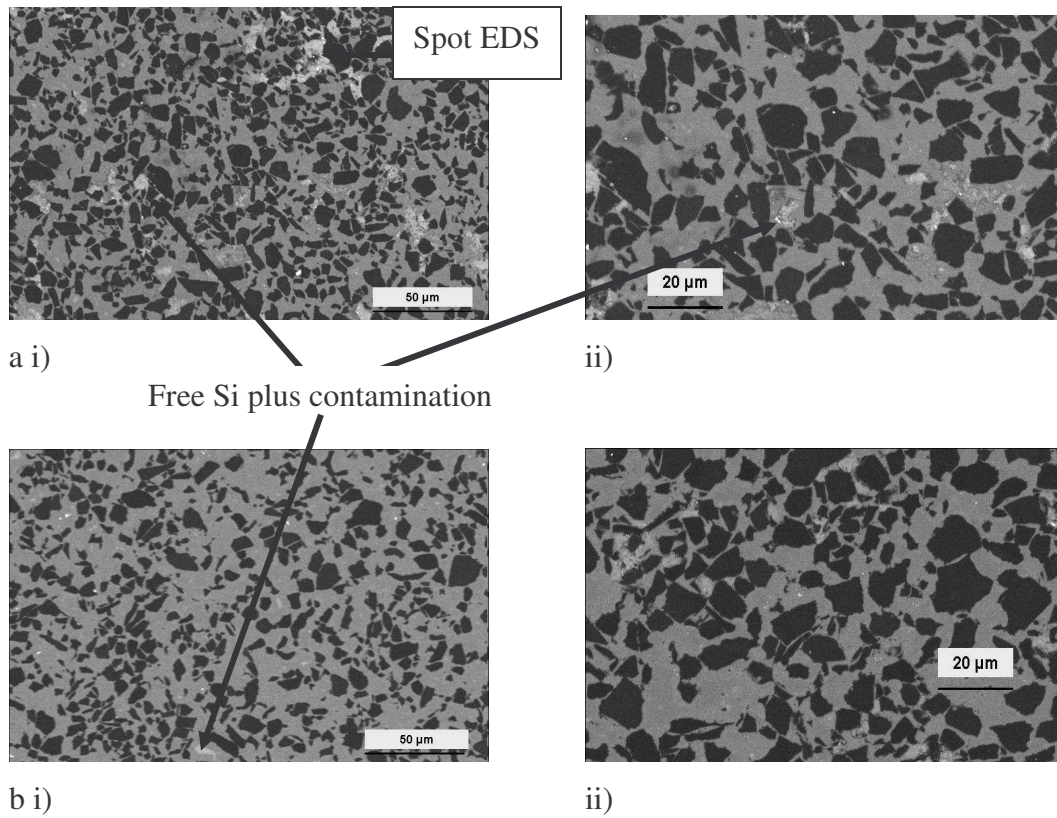


Fig. 7.5: Typical backscatter SEM micrographs of polished cross-sections of D9 diamond (10% resin) preforms infiltrated for 30 minutes at a) 1450°C (vol% composition: D = 49; SiC = 51; Si = 0) and b) 1500°C (vol% composition: D = 53; SiC = 47; Si = 0)

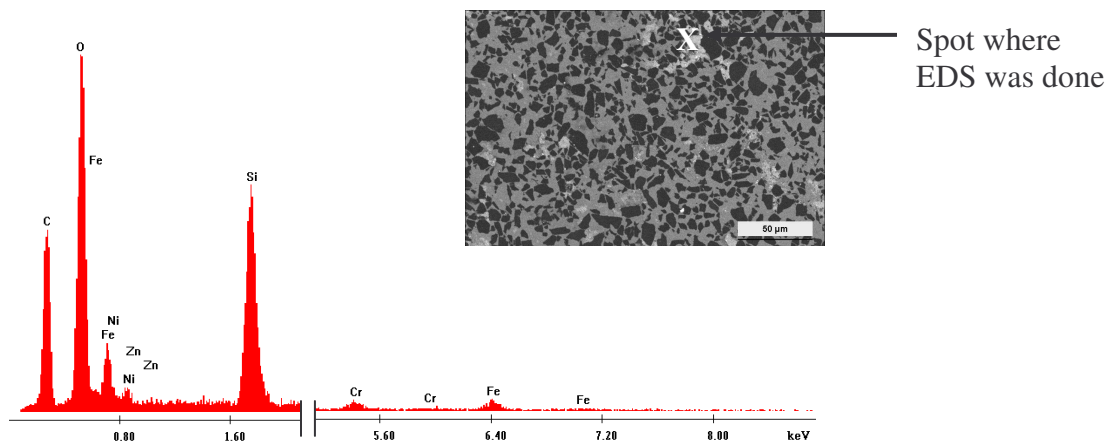


Fig. 7.6: The spot EDS results of a polished sample of D17 diamond produced at 1450°C (fig 7.4a) showing the white phases to be contamination by metals, Fe, Zn, Ni, Cr and oxygen.

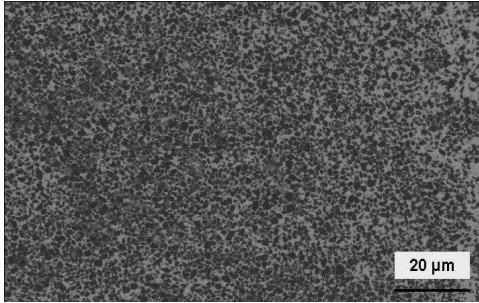


Fig. 7.7: Typical backscatter SEM micrographs of a polished cross-section of D2 diamond (10% resin) preform infiltrated for 30 minutes at 1500°C.

The diamond phase is homogeneously distributed in the D2 final product. There is no observable free silicon phase. The volume fractions of the phases present were analysed to be diamond = 36 vol%; SiC = 64 vol%; Si = 0 vol%.

7.3 Mechanical and wear properties of the produced composite

The D17 diamond preformed with 5% resin (D17R05) was the only one tested for abrasive wear and hardness. An epoxy resin flour was used to abrade the composite material produced (see chapter 3), producing scars that are measured and plotted against time (Fig 7.8). The depth of cut and the feed rate are 1 mm and 0.3 mm/rev respectively, in all the cases. This gives an indication of the wear behaviour of the product. For hardness measurements, the normal indentation method with a diamond indenter at room temperature was followed.

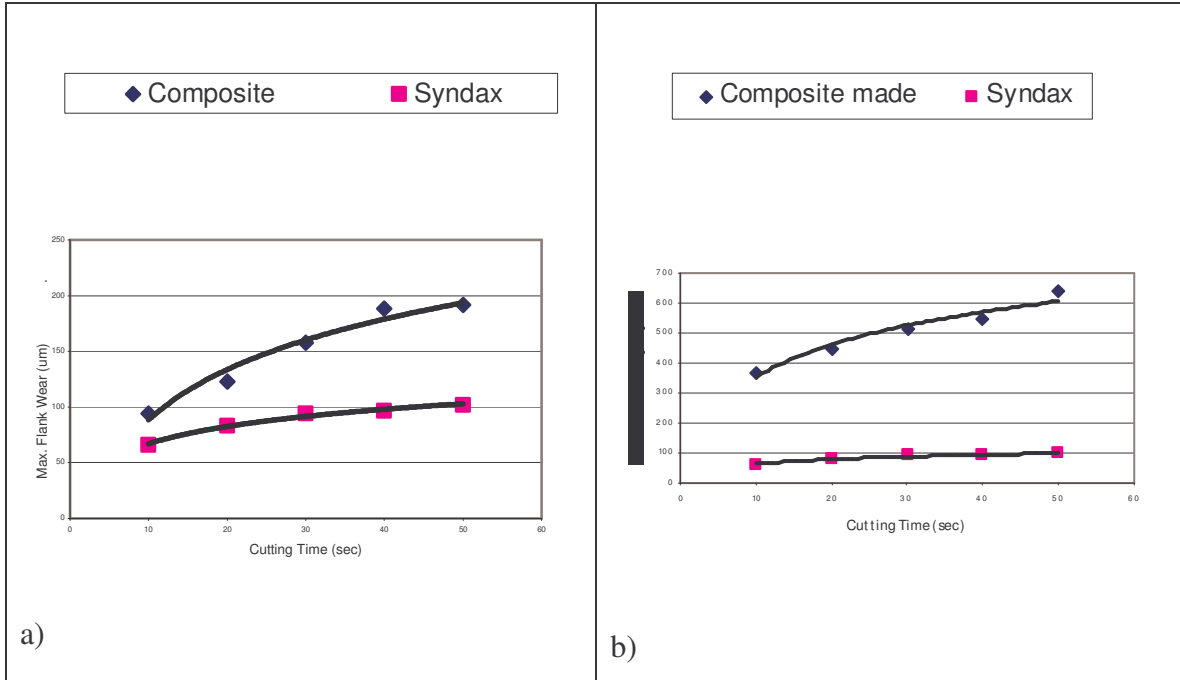
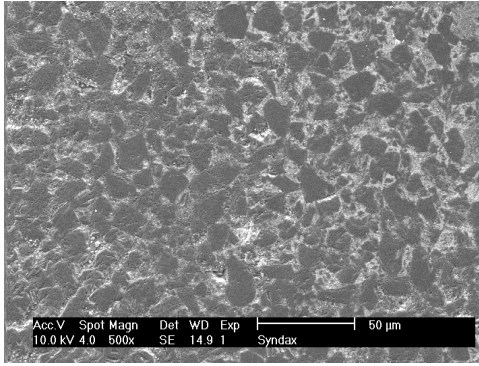
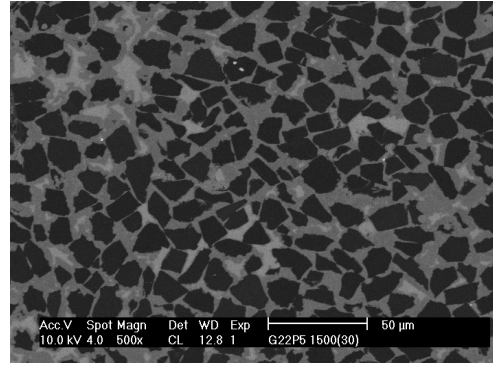


Fig. 7.8: A comparison of the wear behaviour of the composite material made against that of Element Six Syndax-material ($v = 100$ m/min; $DOC = 1$ mm; and $f = 0.3$ mm/rev) at different cutting speeds a) 100 m/min and b) 400 m/min.

Syndax is a type of diamond-silicon carbide composite commercially available and mainly used for wear applications. The difference between the composite made in this work and Syndax is that Syndax is manufactured under high pressure/high temperature conditions, has more than 90 vol% diamond and hence much less binder phase than the composite material produced here. Syndax is made from a multimodal diamond powder whereas the material made here is made from a single grain size distribution of diamond. The diamond grain size in the material of this study is however the same as that of the largest fraction making the syndax material.



a)



b)

Fig. 7.9: A comparison of SEM micrographs of a) Syndax and b) the material made in this work 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 performs much better at the lower cutting speed of 100 m/min than at the higher speed of 400 m/min and its wear resistance at low cutting speed is comparable to that of Syndax. At a higher cutting speed of 400 m/min, the Syndax sample far outperforms the diamond-silicon carbide composite made. The wear scars of both this composite material and syndax were analysed using an OM (optical microscope) after 50 seconds at a cutting speed of 400 m/min and the results are given in fig 7.10 below.

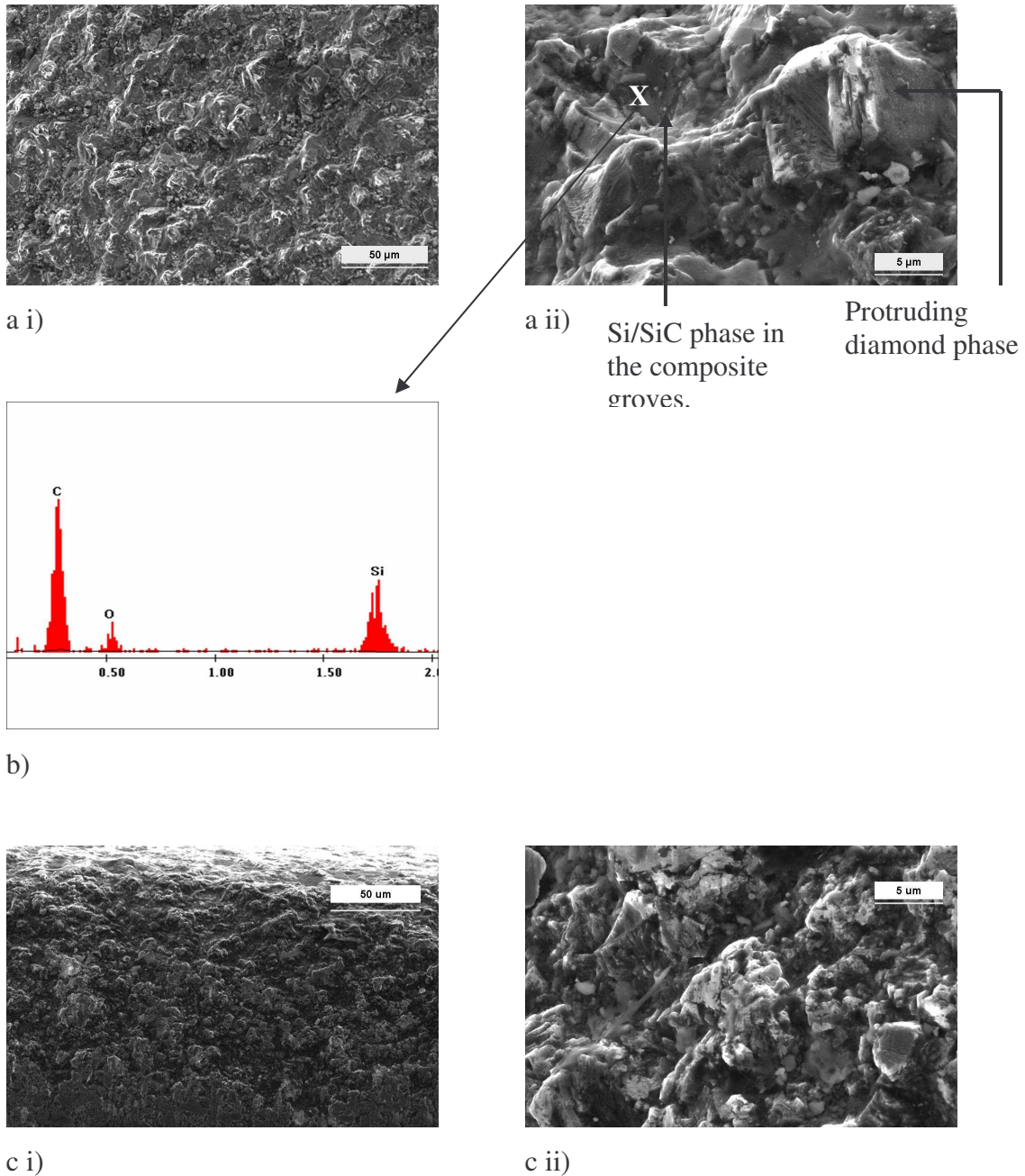


Fig. 7.10: SEM micrographs of the wear scars of a) the composite material made at different magnifications and c) Syndax at different magnifications. b) is an EDS spot analysis on the groove in the material made.

It can be seen in figure 7.10 that there are some protrusions and grooves within the wear scar. The protrusions are diamond particles. The softer phase (Si/SiC) is in the grooves. That phase has been preferentially removed. Some oxygen contamination was also

detected in the grooves, probably introduced through an oxidation process during machining.

It is the main aim of this work to produce an ultrahard material. Besides the determination of the composite's wear behaviour, hardness measurements were also carried out. Hardness was measured using the indentation method. However, only the material made from D17 diamond was indented. After this no more hardness measurements were carried out because the indenter broke.

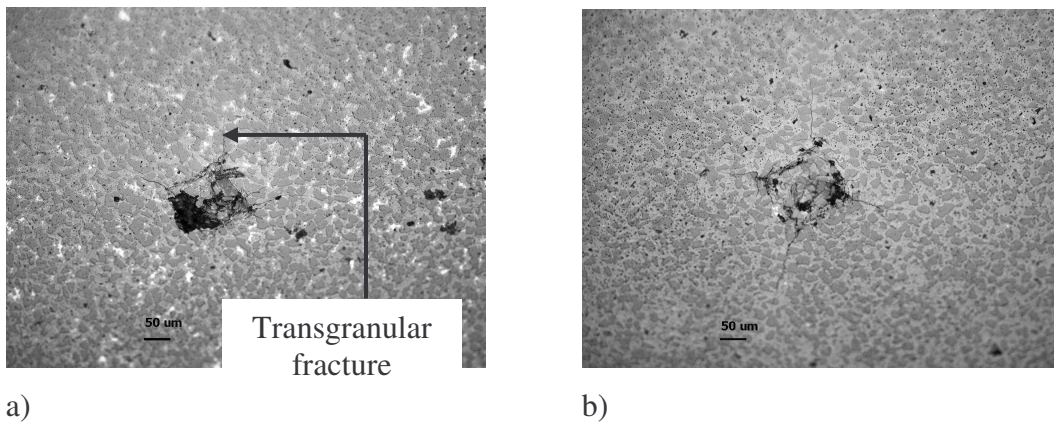


Fig. 7.11: Typical optical images obtained after indentation for hardness measurements.

The indents are not well defined and formed. This is due to the breakage of the diamond indenter during measurements. Initially a load of 5 kg was used for the indentations but no indent could be detected. The load was then increased gradually up to 35 kg. It was only under 35 kg that an indent formed, unfortunately with the concomitant breaking of the indenter. The hardness value could only be estimated to be greater than 35 GPa. The fracture toughness could not be estimated because measuring the diagonals of the indent would be highly erroneous, the fracture lengths also would carry a large error and using such figures in the fracture toughness calculations would be pointless as this value is extremely sensitive to error.

Looking at the nature of the fractures (Fig. 7.11a), one can deduce that the diamond is strongly bound to the matrix because of the presence of some trans-granular cracks.

7.4 DISCUSSION

In this section is presented the discussion of the results of producing the composite by infiltration. The most important factor that influences the infiltration is the right combination of overall porosity and mean pore diameter. When either is wrong, infiltration fails.

The pore diameter in the green compact increases with increasing resin content. The increase in the pore size upon increasing the resin content at least up to 10 wt%, is the major contributor to the improvement of the infiltration observed. As predicted by the Washburn equation,

$$x^2 = \frac{\gamma_{LV} \cos \theta}{2\eta} \cdot R_c \cdot t \quad [1]$$

increasing the pore radius is supposed to increase the rate of infiltration in the absence of a reaction taking place. However, as the reaction product forms, the infiltration rate decreases until a point where it terminates due to pore closure.

Infiltration depths and the flow in table 7.2 have been estimated. For the D2 with a pore size of 0.57 μm , in the absence of a reaction one can expect a higher infiltration depth.

Table 7.2: Estimated infiltration depth at 1500 °C that could be expected for the diamond preform D2R05 used in this work in the absence of any reaction.

Preform	Pore size (μm)	Estimated flow Rate constant (m^2/sec)	Expected infiltration height (mm)	Expected time to full infiltration (sec)
D2R05	0.57	3×10^{-4}	5	1.7×10^{-2}

Naturally however, a decrease in the infiltration front velocity with increasing infiltration time is expected [2] therefore the flow rate does not remain constant. An enhanced flow retardation happens with time due to the SiC forming and reduction of the pore size, even more so because SiC formation is accompanied by volume expansion. As the flow rate reduces, so does the attainable infiltration depth. Another problem inherent in this system is that there exists a pore size distribution. The finest pores would close first inhibiting further infiltration.

Washburn equation has limitations in predicting the infiltration height as it assumes a constant pore structure. Erik O. Eiset [3] has modelled the Si infiltration into porous media and observed that infiltration rate constant increases with increasing pore diameter.

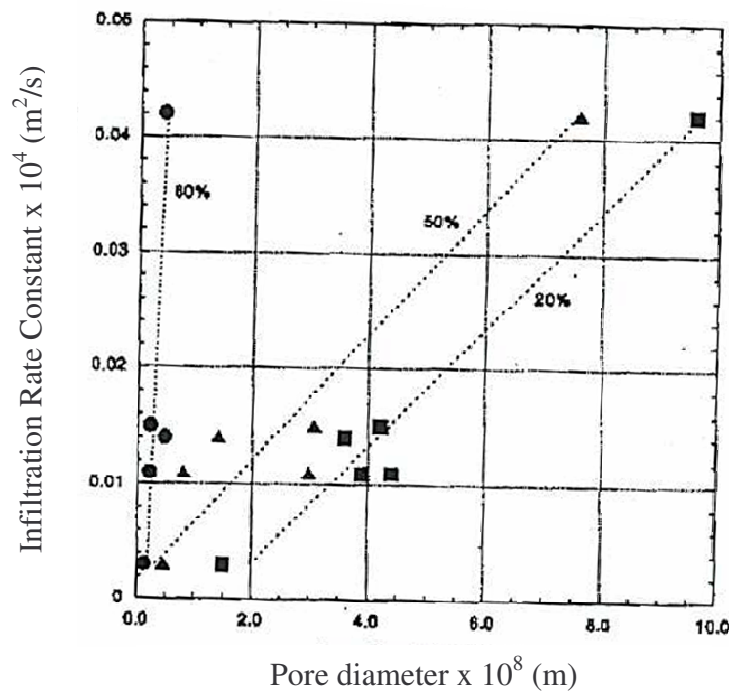
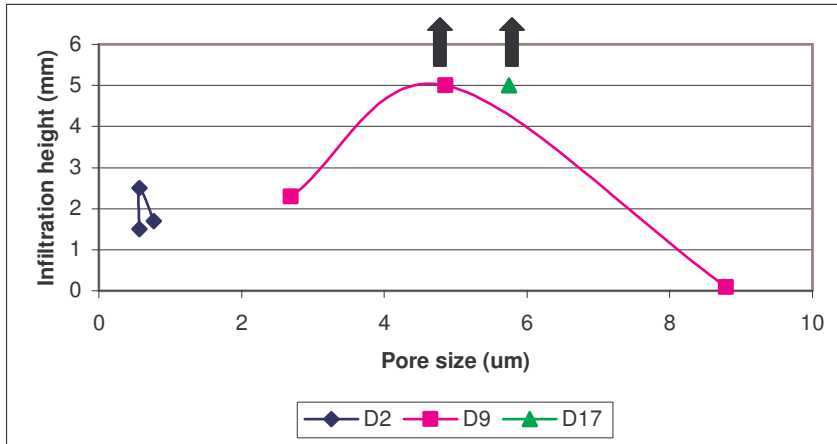


Fig. 7.12: Infiltration rate constant (m²/s) vs pore diameter as defined by 20%, 50% and 80% total infiltration volume. [3]

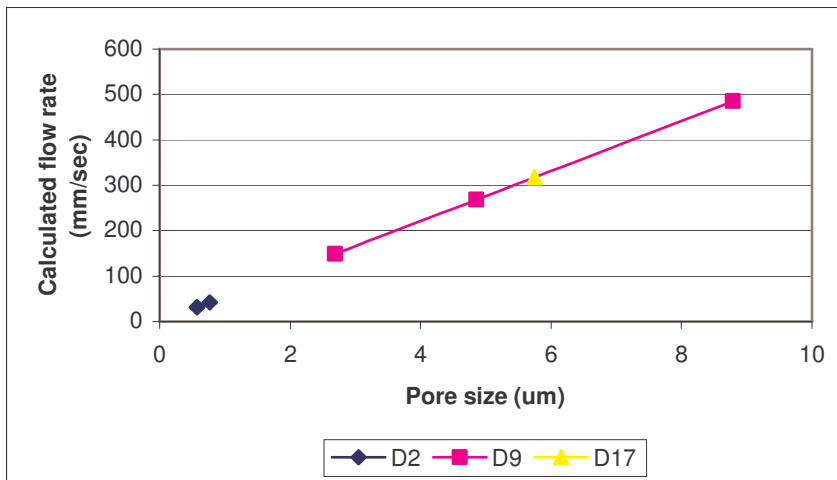
Also, for reactive infiltrations, reactions at the vapour-liquid-solid triple line are believed to affect the final infiltration depth. Evaporation of silicon and carbon in their oxide form (especially when vacuum is used which encourages evaporation even more as in the case

here) changes the inner surface of the pores just ahead of the infiltration front and this changes the chemistry altogether. So, the predicted infiltration heights above could even be further lower if this is taken into account as well as the fact that the product formation is accompanied by volume expansion.

The D2 preform pore size increased from $\pm 0.57 \mu\text{m}$ at 5% and 10% to $\pm 0.7 \mu\text{m}$ at 20% (see table 7.1). This is an improvement 40%. The D9 preform pore size on the other hand improved from $\pm 3 \mu\text{m}$ to $\pm 5 \mu\text{m}$ and $\pm 9 \mu\text{m}$ upon increasing the resin as in D2. This is an improvement of 67% and 200% respectively. Clearly, the increase in the pore size for the D2 was not good enough to have a large effect on the infiltration depth. The 20% resin containing preforms in both grades showed worst infiltration depths. In fig 7.13a, the D9 pore size that was fully infiltrated approaches that of the D17 (which in this work represents the ideal situation for infiltration under the conditions employed).



a)



b)

Fig. 7.13: Infiltration at 1500 °C for 30minutes a) A plot of infiltration heights obtained against the mean pore size for different diamond grades. b) A plot of the calculated melt flow rates (see appendix) against pore size for the different diamond grades.

It should be noted however that there exists some fine pores as well within the preform across which the melt flow rate drops. From the above calculation, it can be deduced that realisation of a full infiltration is a matter of seconds. Longer dwell times hence may only be employed to drive the conversion of any free Si into SiC.

From figure 4.7a (chapter 4), the nucleation rate of SiC can be estimated. At the ramp rate of 50 °C/min employed, it would take about 90 seconds for the temperature to reach

1500 °C, 60 to reach 1475 °C and 30 to reach 1450 °C, from Si melting temperature (1420 - 1425 °C), and therefore the rate of SiC nucleation is at least 3 µm/min:

4.5 µm/90 sec = ~3 µm/min	at 1500 °C
3.2 µm/60 sec = ~3 µm/min	at 1475 °C and
1.6 µm/30 sec = ~3 µm/min	at 1450 °C

The reaction study at the different temperatures was however done on a constant surface area, the CVD diamond plate. In the case of different diamond grades being infiltrated, it is expected that the surface area changes and so will the nucleation rate which will increase with increasing surface area and hence the grades with finer diamond and finer pores (for example D2) will suffer the reaction choking due to a combination of high nucleation rate and small pore channels.

Ekimov et al [4] employed ultra high pressure in their infiltration experiments (7.7 GPa, 1400-2000 °C), but still the infiltration depth they achieved with 1 µm particles, was no more than 2 mm. An alternative route has to be adopted for the making of the fine grained diamond-silicon carbide composites, for example a modification of the diamond surfaces to retard the formation of SiC so that full infiltration of the preform is attained prior to pore closure. One way to modify this surface is by coating with a thin layer (< 0.5 µm) of SiC.

The large grained product has free silicon in them due to their large interparticle spaces that fill with large amounts of the melt. It then requires longer dwelling times to drive the reaction to completion as the reactants have to diffuse through the SiC to get to each other and further react. Some medium and all fine grained products have no detectable free silicon in them. Their pores are much finer. Shorter interparticle distances mean shorter time required to drive reaction to completion. Another reason could be that the analysed medium and fine diamond grade have more amorphous carbon (because they contain 10% resin) which is expected to react better with silicon than the crystalline

carbon in diamond based on Fitzer and Gadow investigations [5], against the analysed coarse diamond that has 5% resin.

The product has a good wear resistance at low cutting speed (100 m/min) that is comparable to that of Syndax which is a good commercial material. It however fails quickly at high cutting speeds (400 m/min). Since this material is a lot cheaper to produce than Syndax which is made using ultra-high pressures (5 GPa), it can be an excellent competitor of Syndax in applications not involving severe wear conditions.

From the wear scar of the product, it can be inferred that it wears firstly by abrasion of the binder phase which then leaves the hard diamond phase protruding. These diamond protrusions then get pulled out during machining leaving behind some grooves and further exposing more binder phase which again gets abraded thus repeating the cycle. The main culprit hence is the large amount of the binder phase which is prone to attack by abrasion. Low binder phase content in the product (to mimic syndax) could help realisation of a better wear resistant material. However, to realise this, the use of ultra-high pressures has to be considered.

When the wetting and reaction between diamond and silicon (chapter 4) is taken into account, it has been found that the main inhibitor to achieving full infiltration in fine-grained diamond preforms is the fast initial rate of SiC formation. Also, the use of silicon powder could be adding to this problem as well as gases that may be produced during infiltration, which change the surface of the pores.

7.5 CONCLUSIONS

Using resin binder, diamond preforms can be formed. Increasing the resin improves infiltration at least up to 10% resin content. Further increase of the resin results in lower porosity which leads to fast choking by SiC formation, hence an optimum exists for the resin content that improves infiltration.

A maximum of about 2.5 mm infiltration depth was achieved for the D2 diamond with 10% resin. A 5 mm thick D9 preform with 10% and a 5 mm thick D17 preform with 5% resin were fully infiltrated.

The resulting material exhibits good wear behaviour comparable to that of Syndax at a cutting speed of 100 m/min and has a hardness value greater than 35 GPa. The large amount of binder phase in this material is responsible for the fast wear of the material, when compared to Syndax especially at a higher cutting speed.

The phenomenon of reaction-chocking is the one responsible for the difficulty to obtain full infiltration in fine grained preforms. Without the reaction taking place, there would be unlimited infiltration depth achievement within possible manufacturing sizes. Factors apart from reaction rate such as the volume expansion accompanying it, using of powder which oxidises quickly, and possible evolution of gases especially in this case where infiltration is carried out in vacuum that can alter the surface chemistry, also affect infiltration negatively. If low pressure is to be used, an alternative route has to be used to produce fine grained diamond-silicon carbide composites. Perhaps a method of coating the diamond powder with silicon carbide can retard the reaction and at the same time promote infiltration. Longer reaction times ensure the conversion of most or all silicon to silicon carbide if diamond mimics carbon (fig 7.14).

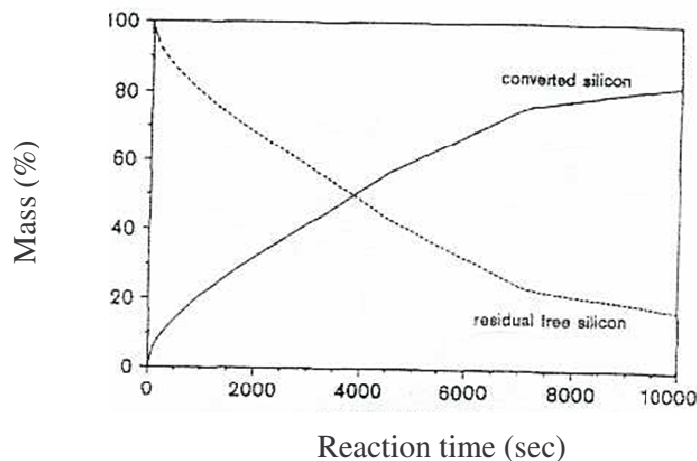


Fig 7.14: Time dependence of silicon conversion from carbon/Si reaction[6]

The green body structure can be changed by changing the compaction pressure, the resin content or the resin properties by using a different type of binder.

REFERENCES

1. Friedrich Raether et al, Oxidation behaviour of carbon short fibre reinforced C/SiC composites, *J. Eur. Ceram. Soc.*, vol 27, 2007, pp 1217-1221
2. P. Sangsuwan *et al*, Reactive infiltration of silicon melt through microporous amorphous carbon preforms, *Met. and Mat. Trans. B*, Vol 30B, October, 1999
3. Erik O. Eiset, Capillary infiltration rates into porous media with applications to silcomp processing, *J. Am. Ceram. Soc.*, vol. 79, no. 2, 1996, pp 333-338
4. E.A. Ekimov, A.G. Gavriluk, B. Palosz, S. Gierlotka, P. Dluzewski, E. Tatianin, Yu. Kluev, A.M. Naletov and A. Presz, High-pressure, high-temperature synthesis of SiC-diamond nanocrystalline ceramics, *Appl. Phys. Lett.*, vol 77, no. 7, August 2000, pp 954-956
5. E. Fitzer and R. Gadow, Investigation of the Reactivity of Different Carbons with Liquid Silicon, *Proc. Int. Symp. on Ceramic Components for Engine*, Japan, S. Somiya, ed., 1983, pp 561-72
6. Frank H. Gern *et al*, Liquid silicon infiltration: description of infiltration dynamics and silicon carbide formation, *Composites part A*, vol. 28A, 1997, pp 355-364