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The low-pressure infiltration of diamond by silicon to form diamond–silicon carbide composites

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Abstract

The infiltration of fine-grained diamond preforms by molten silicon is limited by the blocking of the pores as a result of the volume increase during the reaction of diamond with SiC. Therefore in the present paper the infiltration of preforms made with diamond powders with different grain sizes was investigated. The preforms were prepared using phenolic resin as a binder. With increasing resin content the pore size increases, but the pore volume decreases. As a result the infiltration depth increases strongly for medium resin content. For the fine-grained ~1.5 μm diamond preforms, a maximum infiltration depth of 2.5 mm is obtained at 10% resin, whereas at 5% resin only 1.25 mm could be infiltrated.

Keywords: SiC; Diamond; Composites

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1. Introduction

Diamond is the hardest material known to man. Because of this, it finds extensive industrial application where ultra-hard material properties are needed. Due to its high hardness, it is difficult to make diamond tools of different shapes and sizes purely from cutting and shaping diamond. This has led to the development of diamond composite materials which consist of small diamond grains either sintered together through a liquid phase sintering process, or held together in a matrix by a binder phase material. The former process gives rise to the class of polycrystalline diamond materials (PCD), while the latter results in a number of composite materials, of which the foremost is that of SiC–diamond composites. The introduction of the second phase improves the formability and the fracture toughness of such diamond-based materials.[1]

Metallic phases such as cobalt are present in PCD and are commonly used as liquid phase sintering aids in the production of that material. These metals however were found to catalyze the graphitization of diamond thus limiting the application temperatures of these PCD materials to below 1000 °C.[1] Silicon carbide has been found to be exceptionally good as a diamond binder phase. Because of the structural similarities between diamond and silicon carbide, a strong bond forms between them[2] resulting in a material with a very strong adhesion between the diamond grains and the SiC matrix. Silicon carbide does not react with diamond and the composite material can be used at temperatures above 1000 °C. Application temperature is limited by the melting temperature of silicon if some unreacted silicon is present in the final product.

SiC is commonly formed in situ from a reaction between diamond and/or amorphous carbon or graphite with silicon. The silicon can be introduced into the diamond preforms in different ways, either by infiltrating molten silicon into a diamond preform or by reaction sintering silicon powder and diamond powder.[3–5]

The main production route of these composites includes the use of high-pressure and high-temperature in order to achieve sintering within the regions of diamond stability.[6] Use of high pressures however restricts the range of applications of these materials due to high cost of production and the limited range of possible sizes and shapes of the products made. Some attempts[5] have been made to produce this composite material under conditions of low pressure (i.e. in the diamond metastable region).

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Table 1
The mean particle size of the three diamond grades used in the experiments

Diamond grade	Mean particle size (μm)	
	D (v, 0.5)	D (v, 0.9)
D2	1.51	2.46
D9	9.02	16.42
D17	16.82	22.38

Hot isostatic pressing (HIP) method was employed at a maximum pressure applied of 20 MPa. A product more than 90% dense was obtained. It is of great importance to note that for the reaction sintering route, if the reaction proceeds under low pressure conditions, voids are produced within the body because of the volume reduction occurring during the reaction.[7]

The advantage of infiltration as stated by Qian et al.[2] is that the liquid phase keeps filling the pores in the diamond skeleton and hence a more dense material is produced. Infiltration can also be successfully performed at low pressures giving a dense product.

Infiltration on the other hand has been successful under low pressure conditions only for large grained diamond preforms (7–63 μm grain size).[3,4] It should be noted that in these materials a wide grain size distribution was used. Even under high pressure (7.7 GPa, 1400–2000 °C), Ekimov et al.[8] could infiltrate diamond powder with primary grain size of ∼10 nm but secondary particle (agglomerate) size of ∼1 μm only up to an infiltration depth of 2 mm.

Therefore, the aim of this study is to investigate the infiltration of diamond by silicon using minimal pressure, and to analyze the limitations accompanying the infiltration of small diamond grain size performs.

2. Experimental

2.1. Preform preparation

Preforms were produced using three different diamond powders, labeled D2, D9 and D17 (Element Six (Pty) Ltd). The characteristics of these powders are given in Table 1. The composition of the diamond preforms was modified by the addition of phenolic resin (Plyophen 602N; Fa. PRP Resin). This component was necessary for the formation of the preform during pressing. It acts as a lubricant and a binder. Resin concentrations of 5, 10 and 20 wt% were investigated. The composition and names of the samples are given in Table 2. For the preparation of the preforms phenolic resin was dissolved in acetone (34.3 g/l) and mixed with the diamond powder. This suspension was stirred continuously while kept in a water bath at 70–80 °C to evaporate off the acetone. The resulting powder is agglomerated, the degree of agglomeration increasing with increasing resin content and decreasing diamond particle size. The agglomerated powder is crushed and screened using a −325 mesh screen. The screened powder is pressed into a green compact of 18 mm diameter and 5 mm height under 60 MPa of pressure for about 5 s.

The green compacts were heat treated at 120 °C for 18 h to cure the resin in air. They were then weighed and the resin pyrolysed under argon by heating at a rate of 2 °C/min up to 450 °C followed by 10 °C/min up to 750 °C where a dwelling time of 60 min was undergone. Cooling to room temperature was carried out at a rate of 10 °C/min.

The preforms' green density and porosity were determined after pyrolysis. The green densities were calculated from the mass and volumes of the preforms while the porosity and the pore size distributions were determined using a mercury porosimeter (Quantachrome Poremaster - 60). Raman spectra were acquired with a Jobin-Yvon T64000 Raman spectrometer operating in a single spectrograph mode with an 1800 lines/mm grating. These measurements were performed in order to determine the uniformity of the resin coating. For each sample a line 1000 μm in length and consisting of 100 points was mapped in the central region of the sample using a motorized XY stage.

2.2. Infiltration

An excess amount of silicon powder (1–20 μm Goodfellow) was cold pressed into an 18 mm diameter tablet. This tablet is then placed in an hBN-coated graphite pot (Fig. 1). The diamond preform is placed on top of this Si tablet. Three SiC pieces of 2 mm × 2 mm × 3 mm size are used to separate these two tablets so that no reaction in the solid state, during heating up, can take place. An hBN-coated graphite piston covers the pot. The set-up was heated up at 50 °C/min to 1500 °C at which temperature it dwelled for 30 min. Cooling was achieved at a rate

Table 2
A summary of the infiltration results of the preforms containing different amounts of resin

Sample	Diamond powder	Resin content (wt%)	Weight loss during pyrolysis (%)	Green density (after pyrolysis) (g/cm^3)	Porosity (%)	Mean pore diameter (μm)	Infiltration height (μm)	Phase composition (vol%)		
								Diamond	SiC	Si
D2PR05	D2	5	1.86 ± 0.03	1.82	40	0.47	1250			0
D2PR10		10	4.11 ± 0.01	1.80	29	0.59	2500			0
D2PR20		20	8.73 ± 0.07	1.79	11	0.77	17	36	64	0
D9PR05	D9	5	2.00 ± 0.02	1.84	38	2.7	2000	46	51	3
D9PR10		10	4.10 ± 0.02	1.78	29	4.9	5000[a]	53	47	0
D9PR20		20	9.00 ± 0.03	1.71	15	8.8	97			0
D17PR05	D17	5	2.2 ± 0.2	1.97	25	5,7	5000[a]	52	40	8
D17Pr10		10		2.17	30.2	6.8	5000[a]			

[a] Fully infiltrated.

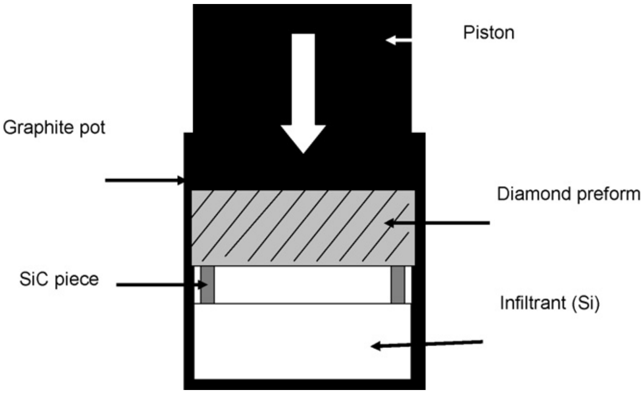

Fig. 1. The set-up for the infiltration experiments.

of 20 °C/min. Pressure (20 MPa) is applied onto the piston after the temperature exceeds that at which silicon melts (1420 °C) to bring the preform and the melt into contact so that infiltration can commence. It is then released when the temperature reaches 1300 °C during cooling.

The products of the infiltration were cross-sectioned. The cross-sections were polished using resin bonded diamond wheels with 1 μm diamond at 3000 rpm before characterization with SEM and XRD.

The phase composition of the infiltrated materials was determined by quantitative image analysis using Image Tool3.

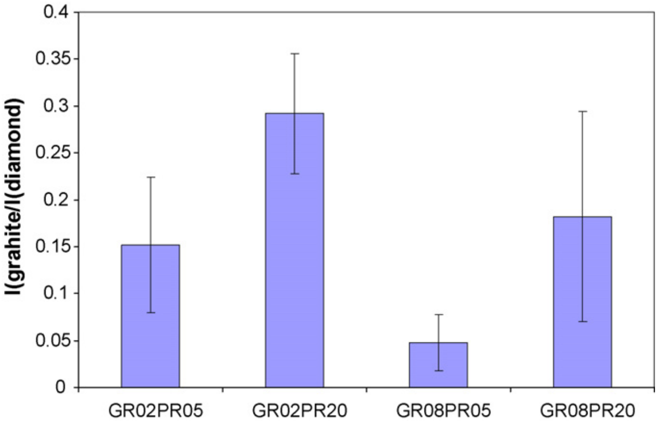

Fig. 3. The average ratio of G-band intensity to diamond Raman peak intensity for the D2 and D9 diamond with initial 5 and 20% resin after their pyrolysis.

3. Results

3.1. Preforms

SEM micrographs of two of the diamond powders used and the powders mixed with the resin are shown in Fig. 2. It can be inferred that the resin coated the diamond homogeneously both before and after pyrolysis. This was confirmed also by the Raman spectroscopy measurements. Fig. 3 indicates that both the materials produced from D2 and D9 which initially had 20%

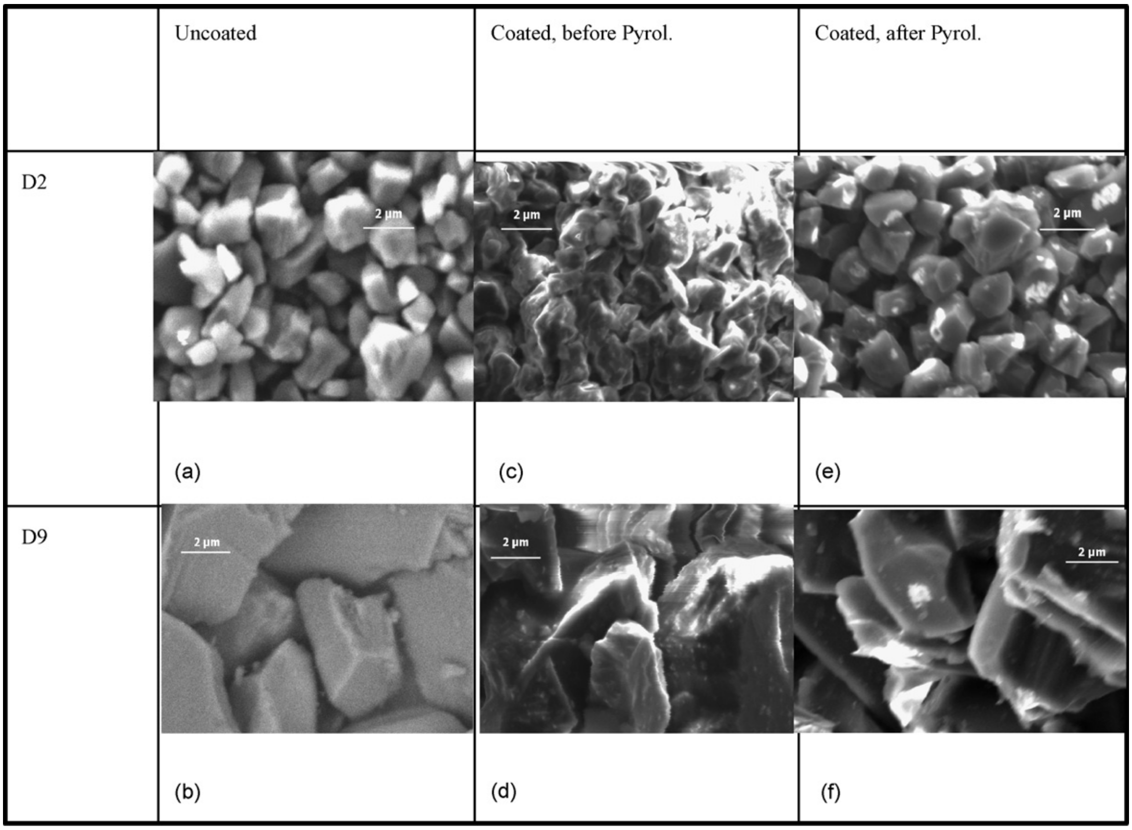

Fig. 2. SEM micrographs of diamond powders D2 and D9 showing the effect of coating the diamond. (a) and (b) is powder before coating, (c) and (d) fracture surfaces of the green compacts before pyrolysis, and (e) and (f) fracture surfaces of the preforms before infiltration.

resin have thicker graphitic carbon layers than their 5% counterparts. The main graphitic carbon G-band gave fairly constant peak intensity in all samples for all the mapped points, indicating fairly uniform coverage by the resin.

The pore size distribution determined by Hg-porosimetry is given in Fig. 4 for the preforms prepared from diamond powder D2 and D9. In Table 2 the green densities and mean pore channel diameter are given. An increase in the resin content increases the average pore diameter while decreasing the pore volume. The decrease of the pore volume is more pronounced for the smaller diamond grain sizes. Nevertheless, the overall green density is nearly constant.

3.2. Infiltration results

The results of the infiltration experiments for the different preforms are given in Table 2. The micrographs in Fig. 5 show the cross-sections of infiltrated samples. The infiltration depth for the different materials is clearly visible. Increasing the amount of the resin in the preforms up to 10 wt% improves the infiltration of the green compacts for the materials produced from the low grain sizes diamonds, e.g. for the material D2Pr05 with 5% resin the infiltration depth was only 1250 μm and increases up to 2500 μm for the material with 10 wt% resin (D2Pr10).

The SEM micrographs of the polished sections (Fig. 6) clearly indicate that the infiltrated areas are completely free of pores and with a high concentration of diamond. This could be confirmed by XRD. While in the coarse grained product the presence of free silicon is obvious (the white phase), this is not detectable for the materials with the medium and fine diamond powders, where one can only see the black diamond phase and the grey SiC phase. The amount of diamond determined by image analysis could be slightly overestimated.

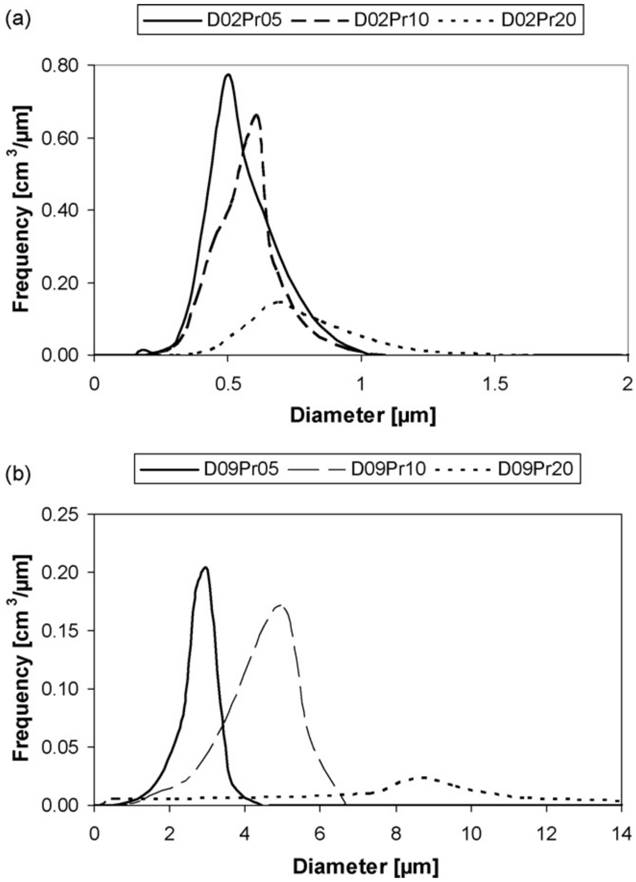

Fig. 4. (a) The pore size distribution in D2 diamond preforms containing 5%, 10% and 20% resin. (b) The pore size distribution in D9 diamond preforms containing 5%, 10% and 20% resin.

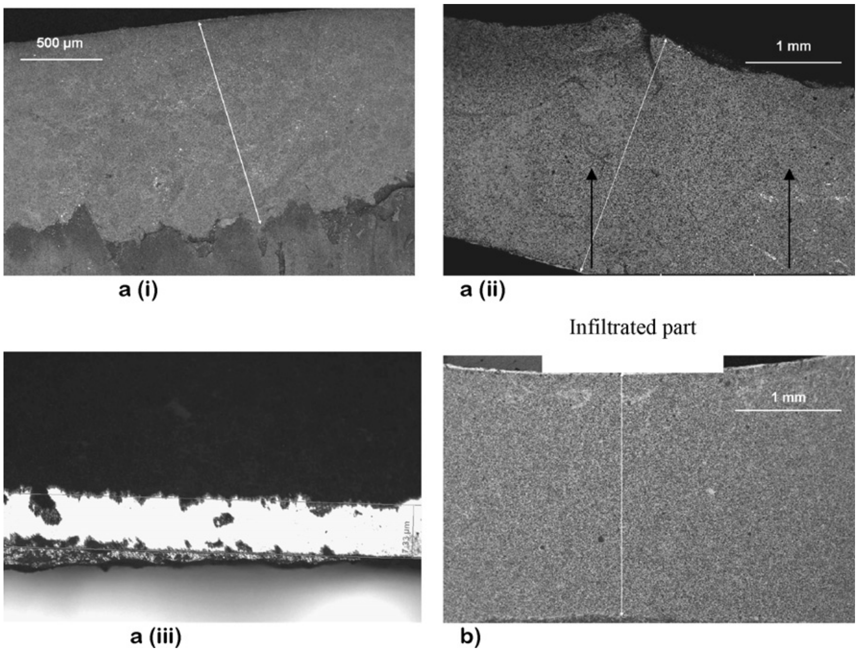

Fig. 5. SEM micrographs showing the infiltration depths of (a) D2 (i) 5% resin, (ii) 10% resin and (iii) 20 % resin, and (b) D9 (5% resin), after infiltration at 1500 °C for 30 min.

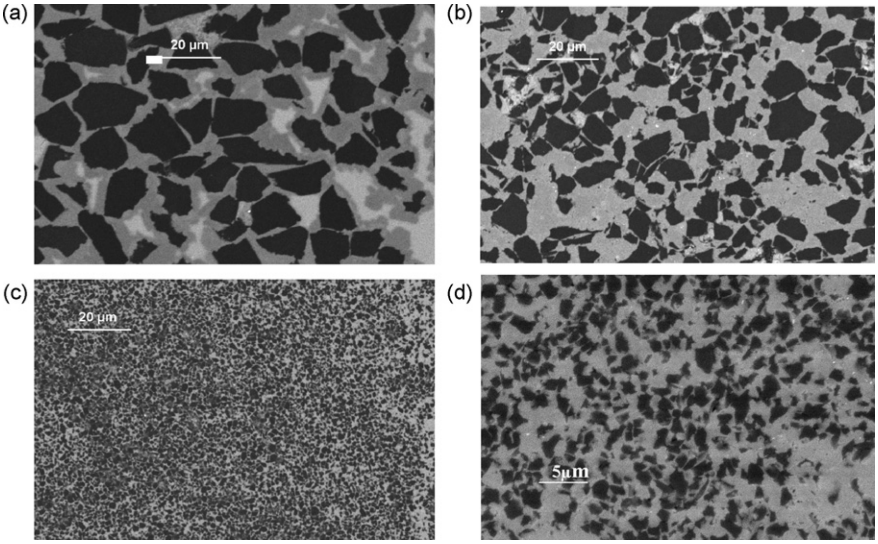

Fig. 6. Typical backscattered SEM micrographs of polished cross-sections of (a) D17 (5% resin), (b) D9 (10% resin) (c) D2 (10% resin), after infiltration at 1500 °C for 30 min. (d) The same as (c) but with higher magnification. The black phase is diamond, the white (where present) is free silicon and the grey phase is SiC.

4. Discussion

As was shown previously[9] diamond is well wetted by liquid silicon at temperatures higher than 1450 °C. Therefore a pressureless infiltration would be possible.

The infiltration is hindered by the formation of SiC surface layers on the diamond, which can block the pore channels and reduce the infiltration depth. Additionally, the silicon will react with the added phenolic resign. The investigations of the reaction of liquid silicon with CVD-diamonds, glassy carbon and graphite has shown,[9–11] that the reaction in all cases results in a very fast formation of protective SiC-layers with similar thickness. The reaction is faster for less crystalline carbon sources. In the infiltrated samples no residual non-diamond carbon was observed. This indicates that the resin converts preferentially into SiC.

The fast reaction of the carbon with liquid silicon results in blocking of the pore channels and is also the reason why infiltration experiments so far were successful only with preforms made of diamonds having large pore sizes.[3–4] The reaction of silicon with diamond or other carbon sources is further enhanced by the strong exothermic character of the interaction of silicon with carbon. This results in a pronounced heat up of the system[10] and an acceleration of the reaction resulting in premature blocking of the pores.

The pyrolysed resin in the sample strongly changes the microstructure of preforms. It increases the pore channel diameter, e.g. by a factor of 1.5 times for D2Pr samples and by a factor of 3 for the samples with the medium grain size (D9).

Unfortunately at the constant pressure used for the preparation of the preforms the pore volume decreases with increasing resin content, i.e. pores between the diamond particles are filled by the pyrolysed resin. The reduction of the pore volume is more pronounced for the low grain size diamond composites (nearly 70%) whereas the change for the samples made with D9 powder it is only 38%. This reduction can be reduced by decreasing the pressure during compaction of the preform.

Small amounts of resin (5 wt%) are needed to make the pressing of the diamond powder possible. Without the presence of resin no pressed samples could be prepared. The resin coats the diamond particles (Fig. 2). This coating plastically deforms during pressing and glues the diamond particles together. With increasing resin content the resin will begin to fill the pores of the preform, during the pressing process, starting with the smaller ones. Therefore only the larger pores will remain and the overall porosity will be reduced. If the diamond particles had a constant packing density in the green body and the resin fills only the pores then the green density had to be increased with increasing resin content. In the investigated samples the density reduces slightly with the increasing resin content. This indicates that the distance between the diamond particles increases with increasing resin content.

To some extend the pore structure in the high resin content materials can be related also to the structure of the granulates prior to the pressing of the preform. However no inhomogeneity of the diamond, Si and SiC distribution was found after infiltration (Fig. 6).

This changed pore structure with increasing resin content will influence infiltration in the following ways:

- The increase of the pore channel radius will improve the infiltration. Therefore for preforms with up to 10 wt% resin content a strong increase in the infiltration depth was observed.
- The reduction of the overall porosity by deposition of the resin between the diamond particles will reduce the infiltration depth due to the possibility of blocking the pores. The volume increase during the reaction of diamond with liquid silicon is much larger than for the reaction of amorphous carbon or graphite with silicon. Therefore, the reaction of the resin with

liquid silicon will result in the blocking of the pores to a lesser extend. This will reduce the influence of the reduction in porosity. It was shown, that carbon preforms with overall densities less than 0.9 g/cm^3 can be fully converted into SiC.[12] Therefore, the resin themselves with a density of less than 1 g/cm^3 can be converted completely. Therefore, the medium resin content improves the infiltration and only high resin content decrease the infiltration due to the lower porosity. Therefore the reduction of the porosity has only a decisive influence on the infiltration at higher resin content (20%).

The study of the interaction of diamond with molten silicon has shown that after the onset of the interaction, a SiC layer of 5–10 μm 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 directly formed would be lower[9] and infiltration would be possible to a higher infiltration depth. A similar effect could be caused by the faster reaction of the pyrolysed resin, which would help improve the infiltration additionally. For the material D22Pr5 after 30 min infiltration the thickness of the SiC-layers formed on the diamonds can be estimated to be in the range of 2–5 μm (Fig. 6a). This value is less than what was observed in model experiment with CVD-diamond plates.[9]

The resin has the additional effect that a smaller amount of diamond is converted to SiC. Therefore high amounts of diamond were observed in our samples after infiltration.

The large grained products contain some free silicon due to their large pores in the preforms. 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.[9,11] The medium and fine grained products have no detectable free silicon in them which is in agreement with this explanation.

5. Conclusion

The investigation of the infiltration of diamond preforms produced from mixtures of phenolic resin and diamond of different grain sizes from 1.5 to 17 μm can be summarized as follows:

(1) The addition of the resin allows a simple shaping of preforms.
(2) Increasing the amount of resin causes pronounced increases of the pore channel diameter and reduces the amount of porosity at similar green densities, because the resin fills partially the space in between the skeleton formed by the diamond particles.
(3) Despite the fact that the overall porosity is reduced by adding the resin, the infiltration depth increases by a factor of two for the D2Pr10 in comparison to the D2Pr05. Similar effects were found for the samples with coarser grain size (D9Pr10).
(4) For a larger resin content the infiltration depth decreases again strongly due to the much lower pore volume.

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References

[1]. Tomlinson, P. N., Pipkin, N. J., Lammer, A. and Burnand, R. P., Indust. High performance drilling-Syndax 3 shows versatility. *Diamond Rev.*, 1985, **6**, 299.

[2]. Qian, J., Voronin, G., Zerda, T. W., He, D. and Zhao, Y., High-pressure, high-temperature sintering of diamond–SiC composites by ball-milled diamond–Si mixtures. *J. Mater. Res.*, 2002, **17**(8), 2153.

[3]. Gordeev S.K, Danchukova L.V., Ekstroem T., and Zhukov S.G. Method of manufacturing a diamond–silicon carbide composite and a composite produced by this method. CA2301775, 1999.

[4]. Gordeev S.K., Zhukov S.G., Danchukova L.V., and Ekstrom T. Method of manufacturing a diamond–silicon carbide–silicon composite and a composite produced by this method. EP1253123, 2002.

[5]. Shimono, M. and Kume, S., HIP-sintered composites of C (diamond)/SiC. *J. Am. Ceram. Soc.*, 2004, **87**(4), 752.

[6]. Hall, H. T., A synthetic carbonado. *Science I*, 1970, **169**(39), 865.

[7]. Hillig, W. B., Making ceramic composites by melt infiltration. *Am. Ceram. Soc. Bull.*, 1994, **73**(4), 56.

[8]. Ekimov, E. A., Gavriliuk, A. G., Palosz, B., Gierlotka, S., Dluzewski, P., Tatianin, E., Kluev, Y., Naletov, A. M. and Presz, A., High-pressure, high-temperature synthesis of SiC–diamond nanocrystalline ceramics. *Appl. Phys. Lett.*, 2000, **77**, 954.

[9]. Mlungwane K., Sigalas I., Herrmann M., and Rodriguez M., The wetting behaviour and reaction kinetics in diamond–silicon carbide system. Submitted for publication in diamond and related materials.

[10]. Sangsuwan, P., Tewari, S. N., Gatica, J. E., Singh, R. N. and Dickerson, R., Reactive infiltration of silicon melt through microporous amorphous carbon preforms. *Metall. Mater. Trans. B*, 1999, **30B**, 933.

[11]. Zhou, h. and Singh, R. N., Kinetics model for the growth of silicon carbide by the reaction of liquid silicon with carbon. *J. Am. Ceram. Soc.*, 1995, **78**(9), 2456–2462.

[12]. Siegel, S., Petasch, U. and Boden, G., Biogene Keramik – eine Alternative? *Keramische Zeitschrift*, 2004, **4**, 234–238.