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ScienceDirect
Ceramics International 35 (2009) 2435–2441
CERAMICS INTERNATIONAL
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The wetting behaviour and reaction kinetics in diamond–silicon carbide systems

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Received 15 October 2007; received in revised form 30 September 2008; accepted 6 February 2009
Available online 11 March 2009

Abstract

The wetting behaviour of silicon on diamond and the interaction of diamond with molten silicon were investigated. It was found that diamond is well wetted by molten silicon reaching a contact angle of about 20° after melting. The wetting is caused by the rapid formation of a SiC interlayer by nucleation of silicon carbide grains on the surface of the diamond. Investigations of the interaction of silicon with CVD diamond, using SEM, showed that the initial rate of SiC formation is very fast and is significantly reduced after the formation of a 4–6 μm thick dense SiC interlayer. At that stage further growth is likely to be controlled by the diffusion of Si and C through the grain boundaries of the silicon carbide interlayer. The results were compared with the interaction of silicon with glassy carbon.

Keywords: A. Sintering; B. Composites; D. SiC

1. Introduction

Diamond–silicon carbide composites have been widely produced because of their attractiveness as ultra-hard materials [1–3]. There are two different known routes of production of these composites:

- Mixing of Si with diamond and densification of the mixture under pressure (reaction sintering) [4].
- Infiltration of a preform made from diamond powder or from mixtures of diamond with graphite or resin [5].

The analysis of the literature shows that fully densified materials from the first route could only be obtained under high-pressure high-temperature conditions (8 GPa, 2000 °C) [4]. The use of high or ultra high-pressure limits the application of these materials due to production costs and sizes and shapes accessible with this technique. Under low-pressure conditions (Hot Press and Hot Isostatic Press) the volume decrease during the conversion of Si and diamond into SiC results in some residual porosity. Therefore, a pressure high enough for densification of the reacted compact under diamond stable conditions is necessary.

Infiltration on the other hand has been successful under low-pressure conditions only for large grained diamond preforms (5–250 and 7–63 μm grain size) [5,6]. 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. [3] 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.

Silicon carbide formation, taking place during infiltration, is accompanied by volume expansion of the solid phase. This reduces the size of the pore channels and could result in blockage thereof. This becomes especially a matter of concern in the case of fine-grained preforms [7] which would be of interest for the manufacture of high performance composites. A

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0272-8842/$34.00
doi:10.1016/j.ceramint.2009.02.019

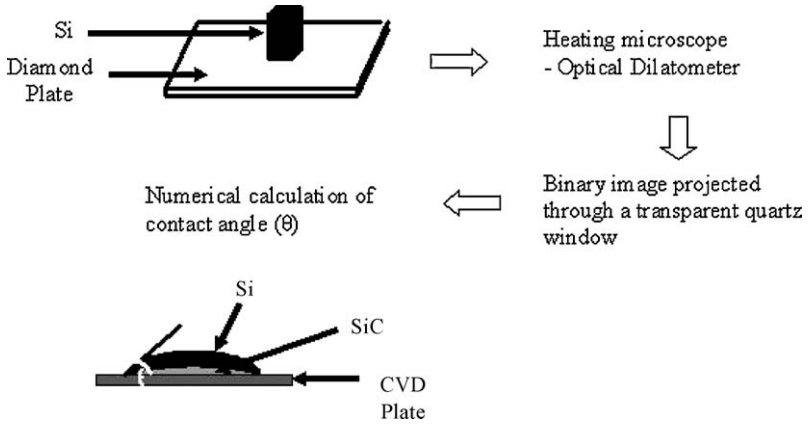

Fig. 1. An illustration of how the wetting angle was determined using a heating microscope.

better understanding of the processes taking place during infiltration (wetting and reaction kinetics) therefore, is necessary.

There exist several papers dealing with the reaction of graphite and glassy carbon with silicon [8–10], but no detailed study of the interaction of diamond with Si has been reported so far. The main focus of this paper therefore is to study the wetting of diamond by Si, and the formation of SiC interlayer by the reaction of liquid Si with diamond.

2. Experimental

2.1. Wetting behaviour

Wetting experiments were carried out using a heating microscope optical dilatometer (EMI2). Equipment is calibrated with a certified Pt/Rh 6/30 thermocouple twice a year, inserted in the sample holder, by using melting points of different standards. A piece of silicon with approximate dimensions of 2 mm × 2 mm × 3 mm was placed on top of a CVD diamond plate (Fig. 1), and heated at a rate of 2 °C/min up to 1550 °C under argon. The silicon–diamond plate assembly is sideways monitored by the microscope and the picture obtained is digitized and shown as a black image against a white background. Cross-sectional real size images of the set-up were taken every 50 °C initially (from 0 to 1000 °C), then at either the same interval or whenever a change is detected by the program. The program determines the contours of the objects being monitored and recognises any changes in the silhouette during the continuous measurement and imaging. From this silhouette, the contact angles are calculated numerically every 10 s.

For comparison, the wetting angles of graphite by silicon, within the same temperature range and conditions were also determined.

2.2. Reaction of silicon with diamond

For the investigation of the reaction, one or more silicon wafers of approximate dimensions 0.5 mm × 5 mm × 5 mm was placed on top of a CVD diamond plate. The diamond plates were obtained from Element Six (Pty) Ltd. They had an average Ra value of 0.134 ± 0.005 μm and average grain size of ∼20 μm, as shown in Fig. 2. This assembly was placed in a graphite pot and covered with a graphite lid coated with hBN (Fig. 3). The samples were heat treated at 1450, 1475 and 1500 °C for different times from 0 min up to 150 min. The heating rate up to the isothermal temperature was 50 °C/min. After reaction the samples were cross-sectioned and polished. SEM micrographs were taken from the cross section. For the

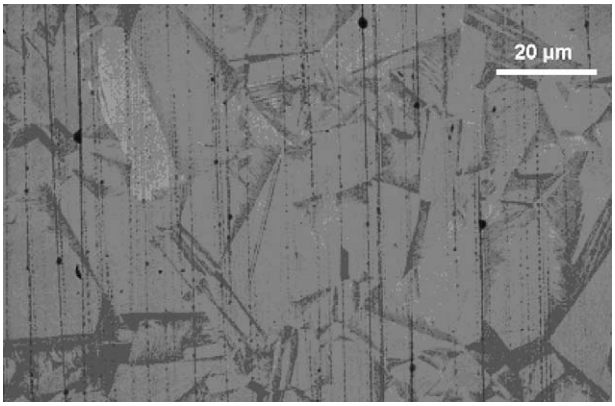

Fig. 2. An SEM micrograph in secondary electron mode of the CVD diamond used for the reaction experiments.

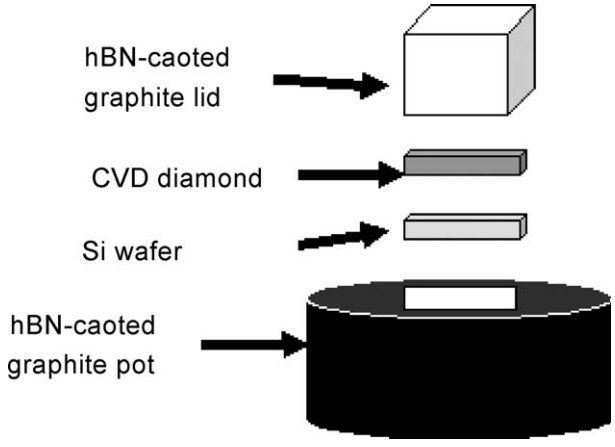

Fig. 3. The set-up for the reaction kinetics determination experiments.

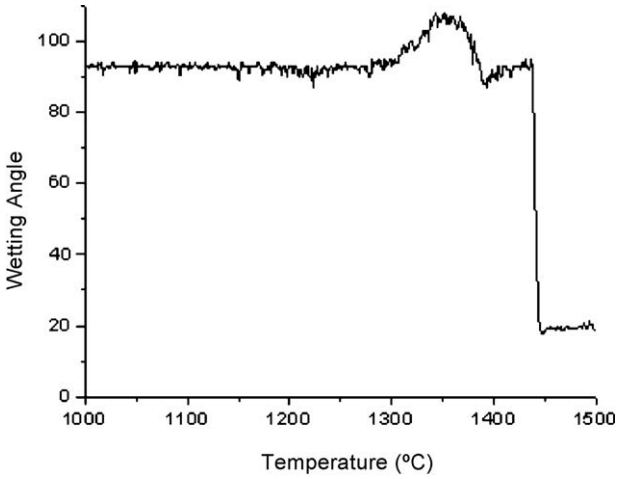

Fig. 4. Apparent wetting angle of silicon with diamond as a function of temperature.

determination of the thickness of the SiC layer formed, 10 micrographs obtained at 1000× magnification were used per sample. The thicknesses of the formed SiC layers were calculated by dividing the area of SiC by the length parallel to the interface layer. After reaction, all samples showed the presence of unreacted silicon on top of the SiC layer formed.

The roughness of the interface between the diamond and the formed SiC was also measured using Image Tool version 3 by dividing the actual tortuous length by the length parallel to the interface.

3. Results

3.1. Wetting

The measured wetting angles as a function of temperature are shown in Fig. 4a for the diamond. The images of the cross sections at different temperatures for the wetting of diamond and graphite by silicon are given in Fig. 5.

An increase in the wetting angle of diamond by Si around 1350 °C (Fig. 4) is due to the silicon minimising its surface energy which becomes possible due to the increased diffusion

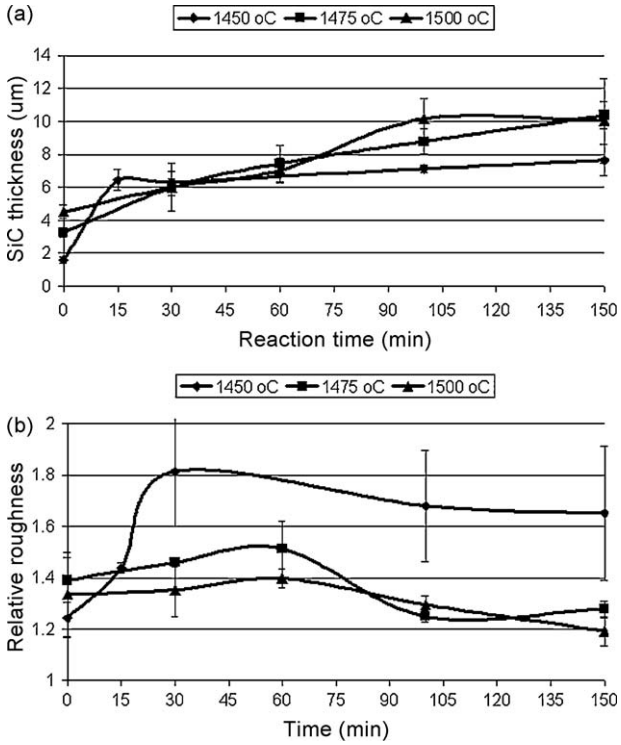

Fig. 6. Dependence of the thickness of the formed SiC layer (a) and the roughness of the interface (b) on the reaction time at different temperatures, 1450, 1475 and 1500 °C.

rates near the melting point [17] After Si has melted, the contact angle drops to below 20°.

The drop down of the wetting angle occurs at 1435 °C. This is slightly above the melting point of silicon (1412 °C). This delay with regard to the melting point could be connected with the kinetics of the process (see Fig. 5f), the destruction of a possible thin oxide surface layer or a slight error in the temperature measurement. The drop of the wetting angle in the case of wetting graphite by silicon takes place earlier (1425 °C). This indicates some kinetic reasons for the shift of the temperature at which the wetting angle drops down rather than a non-perfect calibration of the temperature. The

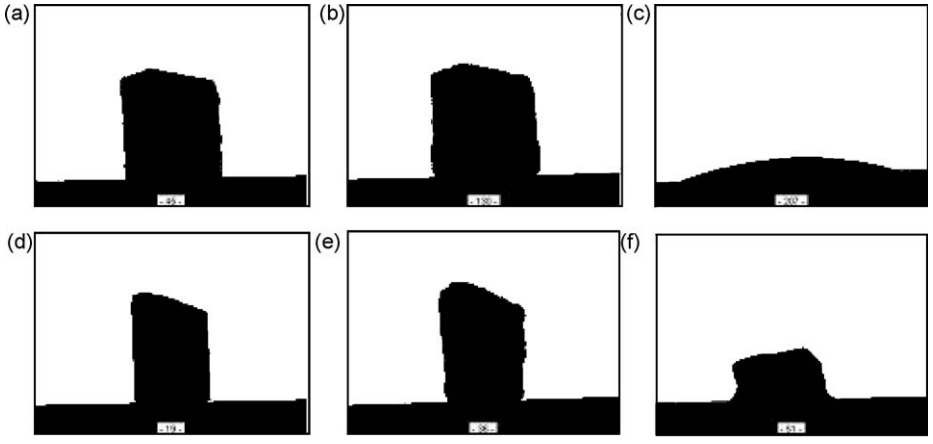

Fig. 5. The contact between diamond and Si at (a) 1000 °C; (b) 1350 °C; (c) 1500 °C; and between graphite and silicon at (d) 1000 °C; (e) 1350 °C; and (f) 1429 °C.

observed wetting angles between 1412 and 1435 °C are rather kinetically determined and are not the equilibrium ones. The resulting wetting angles after melting the silicon are given in Table 1.

3.2. The interaction of Si with diamond

The Si/diamond reaction couples were heat treated at 1450, 1475 and 1500 °C at different times. The thicknesses of the formed continuous SiC layer and the roughness of the interface are given in Fig. 6 for the different temperatures and reaction times. SEM micrographs of polished sections of the interfaces are given in Figs. 7–9. The materials reacted at 1450 °C showed some cracks in the Si, which probably are formed during cooling. The SiC layer is not homogeneous but is formed in to well faceted grains. The reaction has resulted in some grooves into the diamond. These grooves are mostly formed at the grain boundaries between the well facetted SiC grains (Fig. 8).

Table 1
The reported wetting angles by silicon on graphite, diamond and SiC.

Material	Temperature (°C)	Contact angle (°)	Literature
Polycrystalline pyrolytic graphitic	1482	5–23	[8]
SiC	1482	30–41	[8]
SiC	1430	38.5	[9]
Graphite	1430	12	This work
	1480	14	
	1480	16	

Even in the samples heated for 0 min at different isothermal temperatures the SiC layer is mostly completely developed (Fig. 8). This indicates the fast growing process of the SiC grains. In these samples (0 min holding time) some SiC-particles are also found in the silicon away from the interface, which were not observed for longer holding times. This

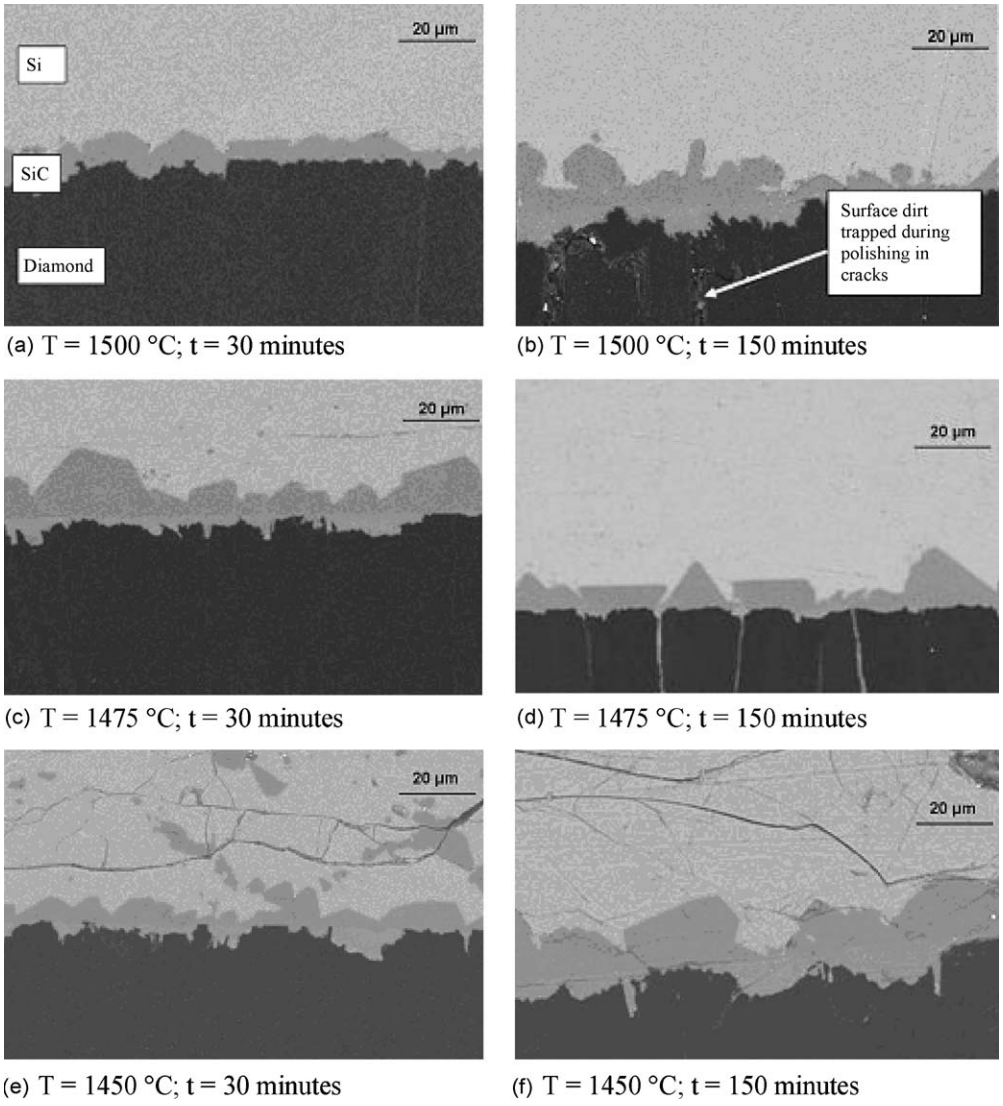

Fig. 7. Backscattered SEM micrographs of the polished cross sections of the diamond/SiC/Si interface as a function of reaction temperature and time. (a) $T = 1500$ °C; $t = 30$ min; (b) $T = 1500$ °C; $t = 150$ min; (c) $T = 1475$ °C; $t = 30$ min; (d) $T = 1475$ °C; $t = 150$ min; (e) $T = 1450$ °C; $t = 30$ min; (f) $T = 1450$ °C; $t = 150$ min.

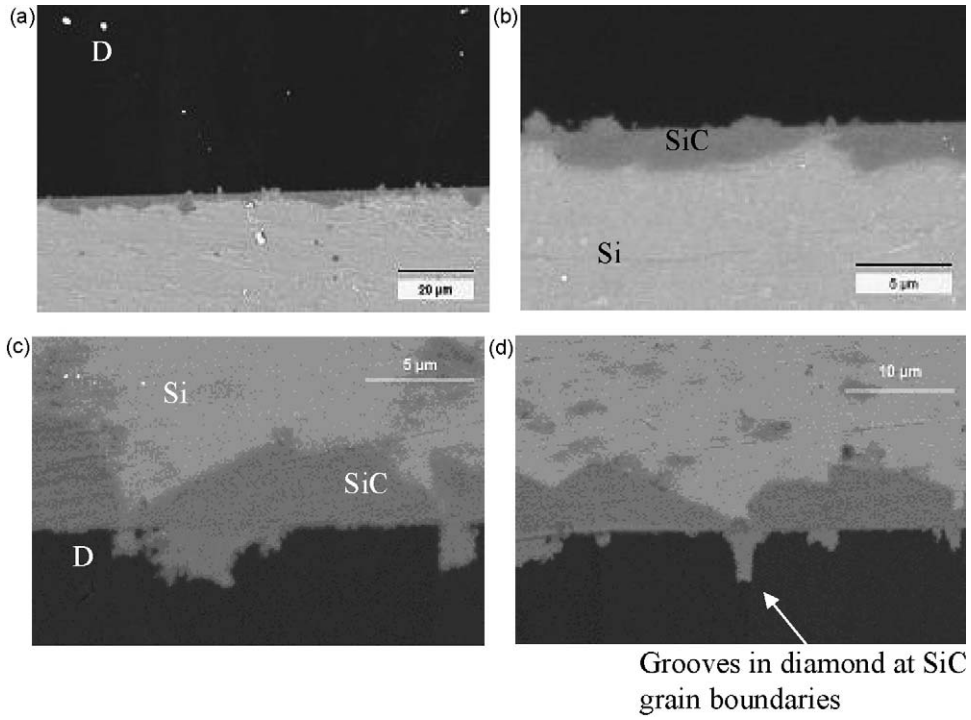

Fig. 8. Backscatter SEM micrographs of cross sections of the polished interfaces showing an ingress of SiC into the diamond by the reaction at the SiC grain boundaries. $T = 1450\ ^{\circ}C$ (a and b) and 1475 °C (c and d) at $t = 0$ min (D = diamond).

indicates the initial rapid dissolution of the diamond in the melt. Similar behaviour was found for the interaction of Si with graphite [8].

The quantitative analysis of the thickness of the formed layer shows the rapid formation of a dense layer, which subsequently grows very slowly. The thickness of the SiC layer increases slightly with increasing temperature. SiC is also formed inside the diamond plate in some of the diamond grain boundaries or in microcracks (Fig. 7d). The diamond–SiC interface, after being leached with Murikami reagent, revealed a difference in the nature of the SiC grains formed during the reaction. While the SiC forming on top of the diamond are large facetted grains

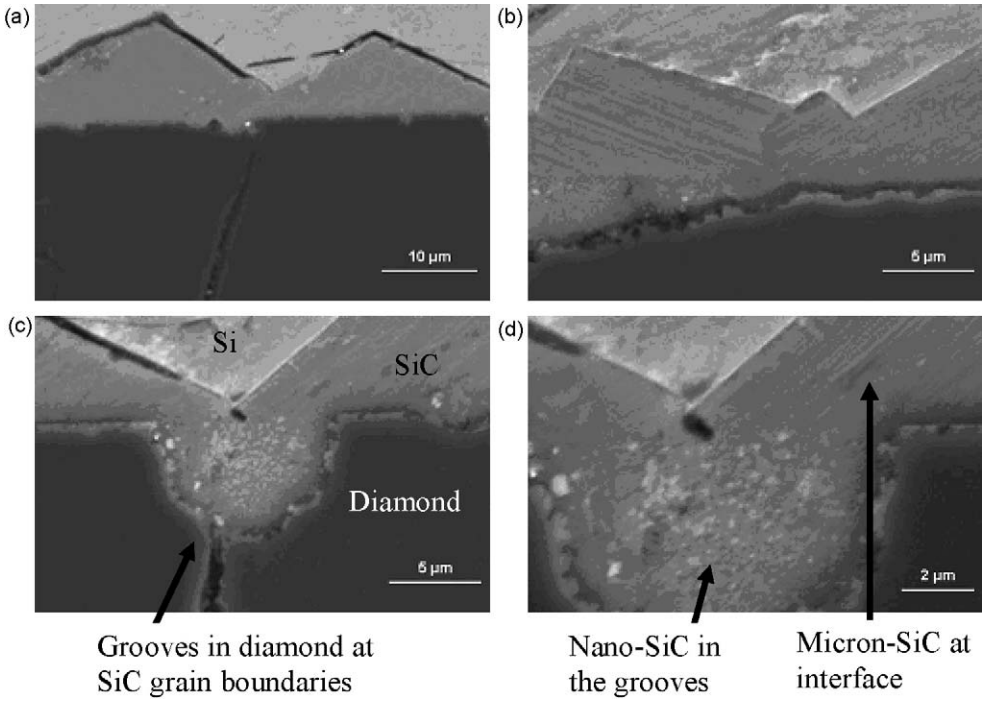

Fig. 9. SEM micrographs of etched cross sections of the sample reacted at 1475 °C for 100 min (the micrographs show different places in different magnifications).

of about 15 μm in length, the SiC forming in the diamond grooves is of submicrometer to nanometer size (Fig. 9).

Although diamond converts into graphite at 1500–1550 °C, there was no evidence of graphite found in all the samples produced.

4. Discussion

The wetting angles observed fit well with the known data from literature for carbon and SiC, see Table 1. Concerning the interaction of Si with graphite it was observed that the good wetting observed is caused by the formation of a SiC interlayer and that the kinetics of wetting is determined by the rate of SiC formation [11]. The higher reactivity of graphite in comparison to that of diamond with Si could explain the reason why the wetting angle of graphite starts to decrease below the melting temperature of silicon whereas the wetting of the diamond starts only at the melting temperature of that metal. The formation of a SiC interlayer also explains the similar wetting angles for diamond and graphite observed above melting. More detailed information about the formation of the SiC interlayer can be obtained from the kinetic experiments.

The dense SiC layer was rapidly formed during the heating up of the reaction couple to the reaction temperature. The morphology of the layer reveals that its formation starts with a few crystals growing along the interface. These grains are well faceted. Similarly faceted grains were also found for the reaction of Si with glassy carbon or graphite [9,11]. These grains, for very short reaction times are isolated [12]. TEM investigations of the interface showed orientation relationships of the diamond and SiC lattice, implying the heterogeneous nucleation of the SiC on the diamond [13]. Based on this information and the observed morphology of the reaction layer formed, it can be concluded that during wetting of diamond by Si at a few positions (distance in the range of 10–20 μm) SiC nucleates and then quickly grows along the diamond surface and into the molten silicon. Between these nuclei (especially at the grain boundaries of the diamond) the silicon dissolves the carbon which is then transported through the liquid to the growing crystals. This explains the quite regular distance of grooves formed at the SiC–diamond interface (Fig. 8). This process is schematically shown in Fig. 10a. The rate of nucleation and the growth rate seem to increase with temperature; therefore the interface becomes less rough during reaction at high temperatures. This would also explain the lower overall thickness at 1450 °C at 0 min reaction time. After the crystals have coalesced, the growth rate is strongly reduced. The growth takes place by the diffusion of Si and C through the grain boundaries. This diffusion process is very slow and therefore the fast reaction at the beginning stops and the overall reaction rate slows down due to the change of the reaction mechanism (transport through liquid to transport along grain boundary).

Zhou and Singh [9] found a similar thickness for the reaction of glassy carbon with silicon in the temperature range 1430–1510 °C, as shown in Table 2. This indicates that the reaction rate of diamond and glassy carbon with silicon is very similar and that the reaction is controlled by some transport processes. These

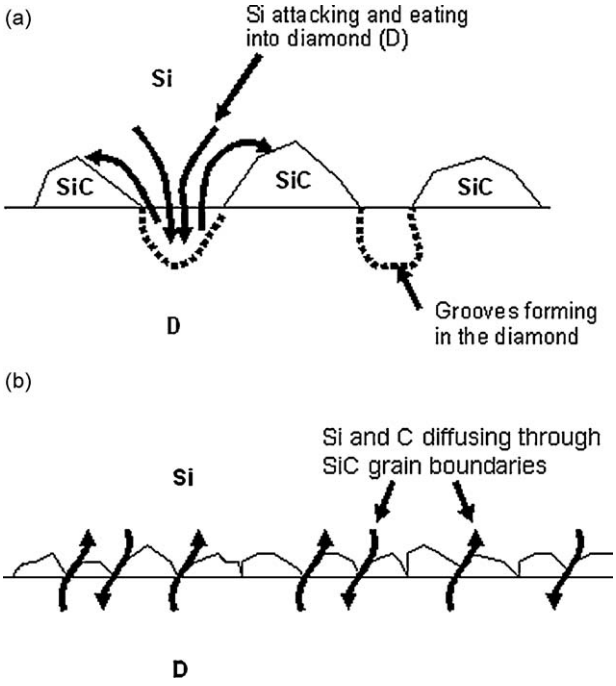

Fig. 10. A schematic showing the formation and growth of SiC at (a) low temperatures and (b) high temperatures.

Table 2
A comparison between results obtained in this study after a 150-min reaction time against those of Zhou and Singh [11] after a 180-min reaction time.

Zhou and Singh [12]			This study		
Temperature (°C)	Thickness (μm)		Temperature (°C)	Thickness (μm)	
	20 min	180 min		20 min	150 min
1430	±10	9	1450	6.5	8 ± 1
1475	±8	9.5	1475	5.0	10 ± 1
1510	±8	10	1500	5.5	10 ± 2

authors proposed a very complicated model including a fourth power rate law. Our results and also a critical analysis of the data in [9] would suggest that there is a change in the mechanism after the layer has formed. Assuming such likely change in the reaction mechanism eliminates the need for a fourth 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. The extrapolation to 1500 °C of the diffusion constants of Si and C in the SiC lattice and grain boundary determined [14,15] for the temperature ranges 1855–2101 °C (for C) and 2010–2274 °C (for Si), resulted in values for C and Si in the lattice of 4.3×10^{-17} and 6.08×10^{-34} cm^2/s, respectively and for C in the grain boundary of 1.11×10^{-09} cm^2/s. These values would suggest that transport would take place only along the grain boundaries in the SiC layer. It is likely from the above micrographs that SiC growth proceeds in both directions, into the diamond as well as into the silicon as suggested by Hillig [16] for the reaction of silicon with carbon, i.e. that a coupling of the carbon and silicon fluxes takes place across the SiC barrier (shown schematically in Fig. 10b).

The micrographs of the etched cross sections (Fig. 9) reveal the existence of much smaller SiC grains in the grooves. From the data it is not possible to decide whether the grains are formed before formation of the SiC layer on the top or after. Experiments with rapid heating may provide an answer to this question.

5. Conclusions

Liquid silicon wets diamond. A wetting angle of approximately 20° could be detected above the melting point of Si. The values of the wetting angle measured are very similar to those observed for glassy carbon or graphite. The wetting is caused by the fast formation of a SiC interlayer. The investigation of the growth of this interlayer has shown that it forms very rapidly (even during the heating up period) by nucleation of SiC grains on the surface of the diamond. After a dense layer is formed the growth rate slows strongly down and further growth is likely to be diffusion controlled (diffusion of Si and C through the grain boundaries). The results obtained can form the basis for the optimization of the preparation of SiC/diamond composites by reactive infiltration.

Acknowledgement

This work was supported by the South African Department of Science and Technology/National Research Foundation Centre of Excellence in Strong Materials and Element Six (Pty.) Ltd.

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