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# Polysilane-derived porous SiC preforms for the preparation of SiC–glass composites

K. LANGGUTH*, S. BÖCKLE, E. MÜLLER
*Institut für Keramische Werkstoffe, TU Bergakademie Freiberg, Gustav-Zeuner-Straße 3, D-09596 Freiberg, Germany*

G. ROEWER
*Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipzigerstraße 29, D-09596 Freiberg, Germany*

Three different types of SiC preforms, with open porosities between 60 and 70%, were prepared by pyrolysis of polysilanes and polycarbosilanes at 1670 K. Some samples of each type of SiC structure were oxidized in air at 1070 K to promote wetting by the glass melt. Preforms were then applied for gas pressure infiltration with an alumosilicate glass melt at 1670 K in 3 MPa argon, and the influence of pore-size distribution and surface composition on infiltration time was investigated. The composition of the precursors was determined by chemical analysis, and pyrolysed SiC was analysed by thermal decomposition. The porosity and pore-size distribution of the SiC-preforms were measured on photographs of sample cross-sections. The SiC–glass composites were examined by light microscopy, scanning electron microscopy and electron scanning microanalysis.

## 1. Introduction

Polysilanes and polycarbosilanes serve as SiC precursors, e.g. for the preparation of fibres [1–5] and mixed carbides [3], and for the densification of porous ceramic preforms by repeated infiltration treatments [6, 7].

The ceramic yield of some of these organic SiC precursors is significantly $< 80$ wt %, and macroporous structures evolve during pyrolysis [3, 8, 9]. In a new approach, this open porosity is considered a beneficial property, because such spongy SiC samples might be suited for composite fabrication by infiltration with slurries or melts, for preparation of macroporous filters [8] or for applications as reservoir materials for salts and liquids [9].

Thus, three different SiC preforms were prepared by pyrolysis of polysilanes and polycarbosilanes, and used for preparation of dense SiC–glass composites by gas pressure infiltration with an alumosilicate glass melt. The objectives of these experiments were to determine the suitability of such SiC structures for the preparation of SiC–glass composites, and to examine the influence of sample properties on infiltration conditions.

## 2. Experimental procedure

Three different SiC preforms were obtained by pyrolysis of four precursors: (1) predominantly meltable “A-I”$^{(*)}$ ($> 60$ wt % will melt); (2) meltable “B”$^{(\#)}$; (3) a mixture of 75 wt % of unmeltable “A-II”$^{(**)}$ with 25 wt % of meltable “C”$^{(\#\#)}$. [“A-I”$^{(*)}$ and “A-II”$^{(**)}$: Poly(methylchloro)silane/-carbosilane, batch numbers PS2-1$^{(*)}$ and PS2-2$^{(**)}$, synthesized at the Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipzigerstraße 29, D-09596 Freiberg, Germany. “B”$^{(\#)}$ and “C”$^{(\#\#)}$: Poly(phenyl)carbosilane, batch numbers DPPPC Me$_3$9$^{(\#)}$ and DPPPC-3C-1.5$^{(\#\#)}$, synthesized at the Fachbereich für Anorganische Chemie 6, Universität-GH-Duisburg, Lotharstraße 6, D-47057 Duisburg, Germany.]

The composition of the SiC precursors, as determined by chemical analysis, is given in Table I. The precursors were ground in a mortar in an atmosphere of dry nitrogen. The particle size of ground “A-II” was between 20 and 400 μm, and the particle shape resembled flat shards.

Conditions of pyrolysis were selected to minimize the pore size of the SiC preforms and to prevent the formation of a closed porosity. Samples were pyrolysed for 1 h at 700 K, 2 h at 920 K and 2 h at 1670 K. The heating rate was 10 K min$^{-1}$, and the atmosphere was flowing argon (2 l h$^{-1}$). Samples for observation of the pore-size distribution were pyrolysed in graphite crucibles $80 \times 25 \times 20\,(10^{-3})$ m (length × width × height). Smaller samples for infiltration with a glass melt were pyrolysed in alumina crucibles $10 \times 10 \times 60\,(10^{-3})$ m.

The SiC preforms were analysed by thermal decomposition: the carbon content was determined by mass spectroscopy of the carbon oxide formed during heating of the sample up to 1770 K in an atmosphere

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* *Postal address*: Altreuthstraße 18, D-91362 Pretzfeld, Germany.

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TABLE I Composition (at %) of precursors "A-I", "A-II", "B" and "C" before and after pyrolysis at 1670 K, ceramic yield (wt %) and composition (at %) of the pyrolysed precursor "B" after oxidation for 2 h at 1070 K

| | C | Si | H | Cl | N | O | Ceramic yield |
|---|---|---|---|---|---|---|---|
| Precursor "A-I" | | | | | | | |
| unpyrolysed | 18 | 13 | 64 | 3 | 1 | 1 | – |
| pyrolysed | 41 | 48 | – | – | 7 | 4 | 70 |
| Precursor "A-II" | | | | | | | |
| unpyrolysed | 18 | 13 | 64 | 3 | 1 | 1 | – |
| pyrolysed | 42 | 48 | – | – | 4 | 6 | 72 |
| Precursor "B" | | | | | | | |
| unpyrolysed | 49 | 4 | 47 | – | – | – | – |
| pyrolysed | 89 | 9 | – | – | – | 2 | 25 |
| oxidized | 3 | 37 | – | – | 1 | 59 | – |
| Precursor "C" | | | | | | | |
| unpyrolysed | 49 | 5 | 46 | – | – | – | – |
| pyrolysed | 77 | 18 | – | – | 1 | 4 | 40 |

TABLE II Composition (wt %) of the alumosilicate glass

| $SiO_2$ | $Al_2O_3$ | CaO | MgO |
|---|---|---|---|
| 60 | 25 | 8 | 7 |

of pure oxygen. The oxygen and nitrogen contents were similarly determined by mass spectroscopic analysis of the decomposition products and measurement of the weight loss during the heating of the sample up to 2270 K in an atmosphere of pure helium. The error of this analysis is $< \pm 3\%$.

Half of the SiC preforms were oxidized for 15 min at 1070 K in flowing air ($10 l h^{-1}$) to promote wetting by the glass melt. Additionally, some preforms of pyrolysed "A-I" and "B" were also oxidized at 1070 K for 2 h to determine the effects of a thick oxide scale on infiltration progress.

An alumosilicate glass with a coefficient of thermal expansion of $3.74 \times 10^{-6}$ $K^{-1}$ and a viscosity of $3.5 \times 10^3$ Pa at 1610 K was selected for the melt infiltration experiments. The composition of the glass is given in Table II.

Infiltration of the SiC preforms with the glass melt was performed in a high pressure, high temperature furnace [Fine Ceramics Technologies (previously KCE-Sondermaschinen), Nikolaus-Otto-Straße 3, 96472 Roedental, Germany]. $Al_2O_3$ crucibles were covered with a thin layer of boron nitride powder to prevent the glass sticking to the crucible. SiC preforms $4 \times 4 \times 50$ mm were placed in the crucibles and covered with broken glass. Samples were heated to ca. 1600 K at a pressure of 3 kPa. The pressure was then gradually increased to 3 MPa argon while the temperature was raised to 1670 K. The time for complete infiltration of unoxidized and oxidized samples was determined by using holding times at 1670 K and 3 MPa argon of 15, 30 and 60 min. The heating rate was 10 K $min^{-1}$ and the cooling rate was 3 K $min^{-1}$.

The SiC samples and the SiC–glass composites were examined by light microscopy, scanning electron microscopy and electron scanning microanalysis.

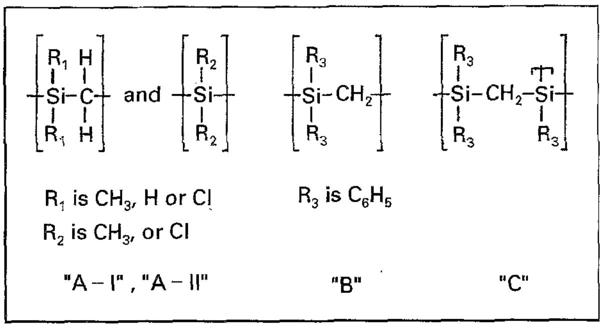

*Figure 1* Schematic structure of the main components of unpyrolysed precursors "A-I", "A-II", "B" and "C".

## 3. Results and discussion

### 3.1. Pyrolysis of the SiC preforms

The schematic structure of the main components of the SiC precursors is given in Fig. 1. "A-I" and "A-II' were mixtures of two different types of polymers, while "B" and "C" were homogeneous materials.

As a result of conditions of synthesis [3, 10, 11], precursors "A-I" and "A-II" were mixtures of poly(methylchloro)silanes and -carbosilanes. "A-I" contained mainly polymer chains and was predominantly meltable at temperatures > 400 K, while "A-II" contained mainly polymers with cyclic cross-linking and was unmeltable [3, 11]. The reason for this difference in melting behaviour was a slightly lower temperature during the synthesis of "A-I" than during the synthesis of "A-II" [10]. Compositions of precursors "A-I" and "A-II", however, were identical within the detection limits of chemical analysis (Table I). The oxygen and nitrogen contents were introduced during synthesis, handling and storage.

The chemical processes during pyrolysis were the same for precursors "A-I" and "A-II" [3, 10, 11]. When thermal energy is supplied, hydrogen, hydrochloric acid gas, methane and carbon oxide are released, and the polymers further interconnect. Beyond 1100 K the polymers consisted only of polycarbosilanes [3]. Formation of amorphous SiC starts > 1270 K, and > 1470 K nanocrystalline β-SiC is detected [3, 11]. Pyrolysis is completed at 1670 K when all hydrogen has been released. The ceramic yield was 70 wt % for precursor "A-I" and 72 wt % for "A-II", and the chemical compositions of the pyrolysed precursors were very similar (Table I). After pyrolysis, the particles of partially meltable precursor "A-I" had connected towards a foamy structure. Particles of precursor "A-II", however, did not connect with each other, and therefore precursor "C" was applied as a binder phase for "A-II".

Precursors "B" and "C" were poly(phenyl)carbosilanes which melt above 400 K, and "C" is a cross-linked variant of "B" [12] (Fig. 1). During pyrolysis, hydrogen, benzene and diphenylenes are released, leaving reactive sites for further cross-linking [12]. The ceramic yield after pyrolysis was 25 wt % for precursor "B" and 40 wt % for precursor "C". Pyrolysed "B" and "C" had high contents in excess free carbon, and oxygen and nitrogen contaminations were introduced during handling and pyrolysis (Table I).

During pyrolysis at temperatures < 670 K, the precursors "A-I", "B", and the mixture of "A-II" and "C", are pliable. The released gases, which constitute the weight loss of the samples, create pore channels on their way out, and an open porosity forms. After pyrolysis, each type of precursor had developed a characteristic, skeletal pore structure, which was determined not only by the amount of pyrolytical gases formed but also by the schedule of the gas release.

## 3.2. Characterization of the SiC preforms

### 3.2.1. Pore-size distribution

The pore channels of the pyrolysed precursors were similar in shape, but different in size distribution. The open porosity, as determined by measuring the pore area on sample cross-sections, was 60% for pyrolysed "A-I", 70% for pyrolysed "B" and 62% for the pyrolysed mixture of "A-II" and "C". The pore size was determined by treating the crooked pore channels as chains of spherical or ellipsoidal pores, and by measuring the largest diameter of each pore. This method was developed to allow a comparison of the pore-size distribution of all three SiC preforms. The error of the measured pore sizes is < 10%. No influence of crucible type on pore-size distribution was observed.

The approximate number of pores per mm$^2$ (pores per $10^{-6}$ m$^2$) was 50 for "A-I", 40 for "B", and 80 for the mixture of "A-II" with "C". The normalized pore-size distribution of the three preforms (Fig. 2) shows that the mixture of "A-II" and "C" had the finest pore structure: 41% of its pores had diameters $\leqslant$ 60 µm, as compared to 23% in the case of "A-I", and 22% in the case of "B" (Table III).

The pyrolysed mixture of "A-II" with "C" had only isolated pores with diameters > 400 µm (0.5% of all pores), while the content of such large pores was 4% in "A-I" and as high as 14% in "B" (Table III).

The pore-size distribution of pyrolysed "A-I" had a small second maximum between 280 and 340 µm pore diameter (Fig. 2). This was the result of the inhomogeneous composition of this precursor, which contained meltable and unmeltable components. Hence, very large pores formed at places which contained only meltable components, for there more pyrolytical gases were released than in regions which contained mainly unmeltable components.

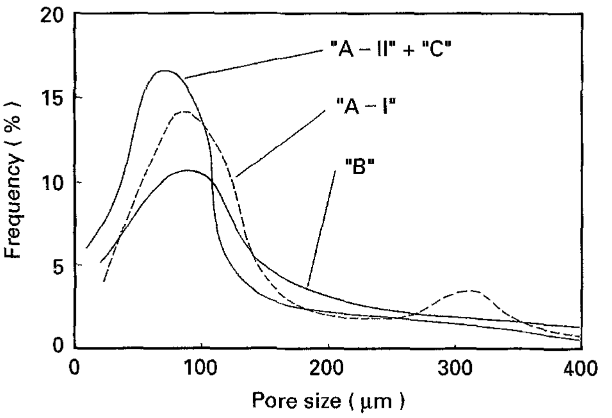

*Figure 2* Normalized pore-size distributions of the SiC preforms pyrolysed from precursors "A-I", "B" and "A-II" with "C".

TABLE III Contents in small and large pores (%) (according to the normalized pore-size distribution, Fig. 2) of the preforms pyrolysed from "A-I", "B" and "A-II" with "C"

| Preform | Pore diameter (µm) | | | |
|---|---|---|---|---|
| | $\leqslant$ 60 | $\leqslant$ 100 | > 300 | > 400 |
| "A-I" | 23 | 51 | 15 | 4 |
| "B" | 22 | 43 | 22 | 14 |
| "A-II" + "C" | 41 | 71 | 4 | 0.5 |

The comparison of the pyrolysed precursors shows that "A-I" and the mixture of "A-II" with "C" had much smaller pores than "B". This was due to the higher ceramic yield of the first two materials, which corresponded to lower amounts of pyrolytic gases. The pore-size distribution of pyrolysed "B" varied locally within each sample, with smaller pores in the lower half (near the contact area to the crucible), and isolated very large pores, up to 2 mm in diameter, in the upper half of the samples. A thin dense crust was observed on the top surface of pyrolysed "B", and apparently this crust had trapped the pyrolytic gases, which then bloated the spongy structure beneath it.

The width of the SiC bridges within the preforms varied between the different types of precursors (Figs 3 and 4) – between 20 and 200 µm both for pyrolysed "A-I" and for the pyrolysed mixture of "A-II" and "C" (Fig. 3). For pyrolysed "B", a very wide range of bridge thicknesses were observed, with fine membrane-like walls of 10 µm size and knot-like walls of up to 1.5 mm in thickness (Fig. 4). The thick walls of "B" often contained cracks (Fig. 4). Thin bridges formed when pyrolytic gases bloated individual pores and then dilated the membranes around them. Thick bridges either formed at spots where only low amounts of pyrolytical gases evolved, or by collapse of pore walls during pyrolysis below 670 K, when the structures were still very pliable.

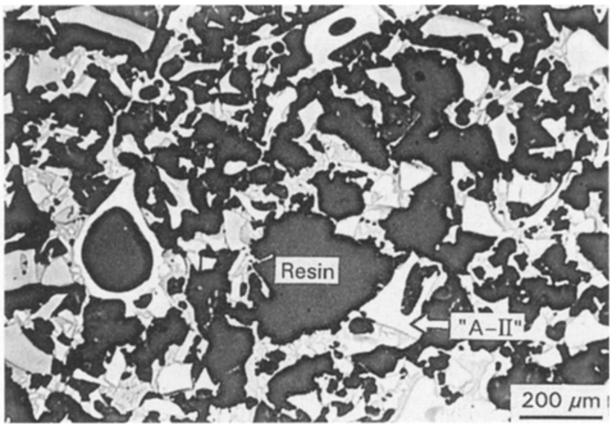

*Figure 3* Pore structure of the pyrolysed precursor mixture of 75 wt % "A-II" with 25 wt % "C"; white "A-II", light grey binder phase "C", dark grey resin.

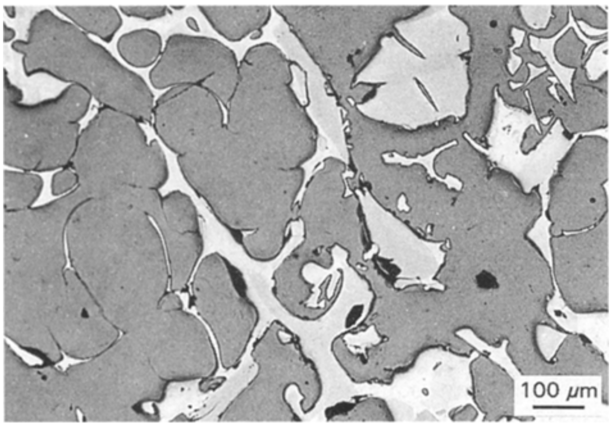

*Figure 4* Thin and thick SiC bridges in pyrolysed "B" (white); cracks in the thick bridge, upper right; grey resin, black pores.

TABLE IV Composition (mol %) of the pyrolysed precursors, and of the pyrolysed and oxidized precursor "B" (2 h at 1070 K), assuming that all oxygen and nitrogen exist as $SiO_2$ and $Si_3N_4$

| | SiC | C | $SiO_2$ | $Si_3N_4$ | Si |
|---|---|---|---|---|---|
| Pyrolysed "A-I" | 91.1 | 0.5 | 4.5 | 3.9 | – |
| Pyrolysed "A-II" | 91.3 | – | 6.5 | 2.2 | – |
| Pyrolysed "B" | 8.9 | 90 | 1.1 | – | – |
| Oxidized "B" | 8.1 | – | 79.7 | 1.1 | 11.1 |
| Pyrolysed "C" | 19.2 | 77.9 | 2.5 | 0.3 | – |

The particles of "A-II" were regularly dispersed in the binding matrix of "C" (Fig. 3), as observed by light microscopy. The compositions of pyrolysed precursors "A-II" and "C" differed significantly (Tables I and IV), thus thermal stresses induced the formation of microcracks between and within both materials. The crack formation was further enhanced by the local variations of the composition of each precursor.

Preliminary experiments had shown that changes in pyrolytical conditions led to increased pore sizes for all precursors. The holding time at 700 K was found necessary to allow the main amount of pyrolytical gases to leave the samples without bloating the pore structure. When this pyrolytical step was performed at 650 K the precursor structures partially collapsed due to their high pliability, while pyrolysis at 750 K increased the final pore size of the structures by > 20%. The pyrolytical step at 920 K allowed completion of the reaction towards polycarbosilanes, and provided further degassing of the samples. The weight loss after the holding step at 920 K was at least 80% of the total weight loss of each sample. When the second pyrolytical holding time was performed at 970 K instead of 920 K, the released gases bloated the pore structure of the samples.

### 3.2.2. Oxidation behaviour

On the surface of all the preforms of pyrolysed "A-I", "B" and "A-II" with "C", which were oxidized for 15 min at 1070 K, a translucent scale of ca. 5 μm width formed. This scale certainly had a lower carbon content than the surface of the unoxidized samples, by loss in excess free carbon or even by formation of $SiO_2$. Samples of "B" had a weight loss of ca. 5 wt % after oxidation, which was probably due to the loss of excess free carbon as carbon oxide. The weight loss of the other preforms was ca. 2 wt %.

When pyrolysed precursors "A-I" and "B" were oxidized for 2 h at 1070 K in air, they displayed a completely different oxidation behaviour. The translucent scale on "A-I", as determined by scanning electron microscopy, had about the same thickness (ca. 5 μm) as on samples after oxidation treatment for only 15 min. Apparently, a dense oxide scale had formed, which protected the samples from further oxidation. However, analytical means for determination of the oxygen content of these scales were not available.

Samples of "B", on the other hand, turned white and fragile after oxidation for 2 h, and their composition, as determined by thermal decomposition, was that of $SiO_2$ with some SiC, $Si_3N_4$ (some as oxynitride) and Si (Table IV). These samples were mechanically weak and unsuited for infiltration with the glass melt, because bridges would partially break. The weight loss of "B" after oxidation for 2 h was ca. 70 wt %. The high content of this material in excess free carbon (Table IV) prevented the formation of a continuous oxide scale on the sample surfaces, which would have slowed down oxidation, as observed in the case of material "A-I".

A supplementary result of the oxidation experiment was a proof of the local variations in composition of such pyrolysed polymers as found on samples of fully oxidized "B". Small spherical pores were observed by scanning electron microscopy (Fig. 5) which had evolved at previously carbon-rich places. The inhomogeneity in composition of this material, however, did not result in a formation of microcracks, as had been observed in the case of the pyrolysed mixture "A-II" with "C".

In an attempt to explain the high weight loss of "B" after oxidation for 2 h and the reduction of the SiC content and the remarkable increase in the $SiO_2$ content (Table IV) the following reaction scheme is proposed:

$$C_{excess} + O_2 \rightarrow CO_2 \quad (1)$$

$$CO_2 + SiC \rightarrow Si + 2CO \quad (2)$$

$$2CO_2 + Si \rightarrow SiO_2 + 2CO \quad (3)$$

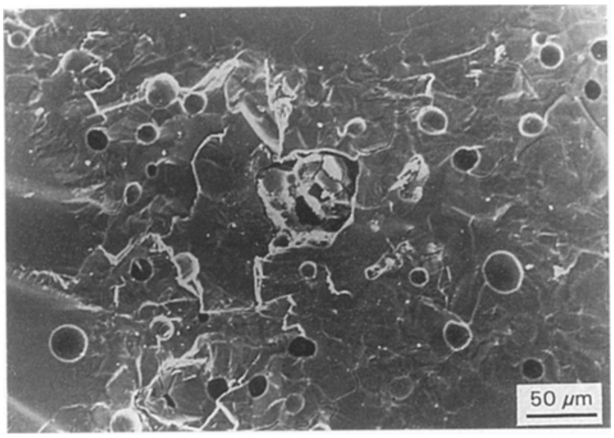

*Figure 5* Pore formation at previously carbon-rich zones of "B" after oxidation at 1070 K for 2 h.

The mechanisms of the oxidation behaviour of pyrolysed "B" remain unknown, as no means for analysis of the reaction products were available, and Equations 1–3 are probably a very simplified description of the processes which actually took place. However, analysis of oxidized samples of "B" by thermal decomposition proved the existence of a significant amount of metal silicon (Table IV), thus a decomposition of the SiC, as suggested in Equation 2, certainly had occurred.

### 3.3. Characterization of glass-infiltrated SiC samples

The time for a full infiltration of the SiC preforms with the glass melt was determined by surface composition, especially by the $SiO_2$ content, and by the individual pore-size distributions.

The oxidized samples of all three types of preforms were infiltrated within 15 min (at 1670 K and 3 MPa argon), so the glass melt entered all samples ($4 \times 4 \times 50$ mm) with an average velocity of at least 8 mm $h^{-1}$. In the case of the oxidized samples, the progress of melt infiltration was apparently determined by the surface composition of the samples, and thus by the wetting conditions. However, no attempt was made to determine the influence of the individual pore-size distributions on infiltration speed by using infiltration times of $< 15$ min.

Unoxidized samples of "A-I" and "A-II" with "C" were fully infiltrated within 60 min at 1670 K [13]; the unoxidized samples of pyrolysed "B" were infiltrated after 30 min. The comparatively fast infiltration of preform "B" was certainly the result of its pore-size distribution being the coarsest among those of the three preforms (Fig. 3). However, the fast infiltration of "B" was also somewhat surprising, because the high content of excess free carbon (Table IV) had been expected to impair wetting of the melt on the preform and thus to slow down the infiltration speed.

The differences in infiltration time between samples differing in wetting behaviour and pore-size distribution may be described by the Washburn equation [14]

$$x = \left[\frac{r^2 t}{4\eta}\left(\Delta P + \frac{2\gamma_{lv}\cos\theta}{r}\right)\right]^{1/2} \qquad (4)$$

with infiltration depth $x$, pore radius $r$, time $t$, viscosity $\eta$, externally applied pressure $\Delta P$, surface tension $\gamma_{lv}$, and contact angle $\theta$.

According to Equation 4, the influence of the pore size and the externally applied pressure on infiltration speed is much higher than that of the wetting angle, as soon as wetting occurs. This is not entirely confirmed by the experimental results of this study, as surface oxidation of the preforms reduced the required infiltration time by up to a factor of four.

After infiltration of the unoxidized samples, the glass was grey at up to 5 mm distance from the SiC. Scanning electron microanalysis of these newly coloured areas in samples of pyrolysed precursor "B" indicated, that carbon had dissolved in the glass. The dissolved carbon was distributed by melt convection, and patterns with layers of dark grey and light grey glass formed in regions where convection had been unrestricted by SiC walls (Fig. 6). Usually, carbon layers form on surfaces of SiC fibres by the following solid state reaction [15–17]

$$SiC + O_2 \rightarrow SiO_2 + C \qquad (5)$$

The mechanisms for dissolution of carbon, or even small carbon particles, in the glass during the infiltration experiments of this study are unknown, but some oxygen was probably supplied by gases dissolved in the glass.

No cracking of the SiC bridges by thermal stresses or reaction with the glass melt was observed in the SiC–glass composites, so all of the three sample types were suited for the melt-infiltration process. Only few microcracks were observed in melt-infiltrated samples of SiC pyrolysed from "A-I" or "C". Such cracks usually formed around the edges of the SiC skeleton due to increase in stress. Numerous microcracks, however, were found in the composites prepared with SiC preforms derived from the mixture of "A-II" with "B".

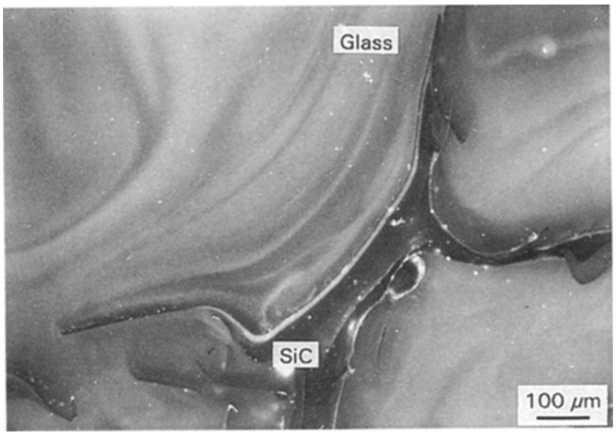

*Figure 6* Layers of dark grey and light grey coloured glass parallel to the SiC surface, as formed by dissolution of carbon during melt infiltration of unoxidized preform "B"; white spots by pores.

These cracks formed mainly due to the pre-existing thermal stresses and microcracks, as discussed above for this type of preform.

## 4. Conclusions

1. SiC preforms suited for gas pressure infiltration with an alumosilicate glass melt were prepared by pyrolysis of polysilanes and polycarbosilanes at 1670 K in argon.
2. The porosity of these samples was between 60 and 70%, and the pore-size distribution and microstructure were characteristic for each pyrolysed precursor material.
3. SiC-bridge curvature and thermal stresses within the preforms (due to local variations in composition) induced the formation of microcracks in the preforms and also in the SiC–glass composites.
4. Wetting of the SiC preforms by the glass melt was promoted by an oxidation step at 1070 K in air.
5. The glass near the surfaces of the unoxidized SiC preforms contained dissolved carbon, which was distributed within the glass by melt convection.

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