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Preparation of Macro-Porous SiC–Al_2O_3 Composites with Polysilanes and Polycarbosilanes

Kathrin Langguth

Institut für Keramische Werkstoffe, TU Bergakademie, Freiberg, Gustav-Zeuner-Straße 3, D-09596 Freiberg, Germany

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Abstract: Spongelike polycarbosilanes with 50% open porosity were prepared by pyrolysis of a mixture of polysilanes and polycarbosilanes at 650°C in argon. Porous SiC–Al_2O_3 composites were prepared by oxidation of the pyrolyzed preforms at 600°C in air and subsequent infiltration with an aqueous Al_2O_3 slurry. Sintering was performed at 1600°C in 1·5 MPa argon. The precursors were analyzed by infrared-spectroscopy and by thermal decomposition. The SiC–Al_2O_3 composites were investigated by light microscopy, scanning electron microscopy, energy dispersive X-ray analysis and electron scanning microanalysis.

1 INTRODUCTION

The application of polysilanes as SiC precursors in composite technology comprises infiltration of porous preforms for an increase in density and mechanical strength,[1–5] synthesis of mixed carbides, e.g. TiC–SiC,[6,7] preparation of nanocrystalline powders[3,7] and preparation of SiC-fibers with different oxygen contents.[3,7–10]

In this study a mixture of polysilanes and polycarbosilanes was pyrolyzed to prepare porous preforms which consisted predominantly of polycarbosilanes. These were coated with an Al_2O_3 slurry and sintered to SiC–Al_2O_3 composites with an open porosity of 20%.

Such macro-porous ceramics may serve as metal melt filters,[11] catalyst carriers[12] or lightweight high-temperature materials.[13]

2 EXPERIMENTAL PROCEDURE

A mixture of 75 wt% SiC-precursor 'A' (poly(methylchloro)silane/-carbosilane, batch number 'PS2', synthesized at the Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipzigerstraße 29, D-09596 Freiberg, Germany) and 25 wt% SiC-precursor 'B' (poly(phenyl)carbosilane, batch number 'DPPPC-3C-1·5', synthesized at the Fachbereich für Anorganische Chemie 6, Universität-GH-Duisburg, Lotharstraße 6, D-47057 Duisburg, Germany) was mechanically ground and blended in a mortar in a dry nitrogen atmosphere. The powdery precursor mixture was filled in graphite crucibles to a height of 10 m^{-3}. The size of the crucibles was 80 × 25 × 25 m^{-3} (length × width × height). Pyrolysis was performed in flowing argon (2 litre h^{-1}) for one hour at 430°C (703 K) and two hours at 650°C (923 K) to obtain the porous structure 'C' which consisted mainly of polycarbosilanes. The heating rate was 10 K min^{-1}. A schematic of the chemical structure of precursors 'A' and 'B' is given in Fig. 1.

The precursors were analyzed by wet chemical analysis and characterized by infrared-spectroscopy, using KBr as carrier material. Mixture 'C' was examined by infrared-spectroscopy before and after pyrolysis at 650°C. Chemical analysis of pyrolyzed pure 'A', 'B' and mixture 'C' was performed by thermal decomposition. During this analysis the carbon content was determined by heating the powdered sample to 1500°C in a pure oxygen atmosphere and measuring the amount of carbon oxide formed by

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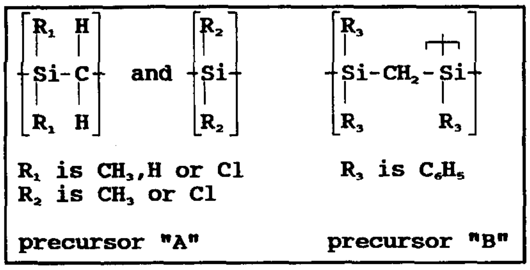

Fig. 1. Schematic structures of unpyrolyzed precursors 'A' and 'B'.

mass spectrometry; the oxygen and nitrogen contents are determined by heating the sample in a helium atmosphere up to 2000°C and analyzing the decomposition products and the corresponding weight loss. The error of this method is less than ± 2%.

The pyrolyzed polycarbosilane 'C' was oxidized in flowing air for 15 min at 600°C for a decrease of the excess carbon in the sample surface and formation of a thin oxygen enriched scale. The oxidized samples were immersed for 5 min in an aqueous slurry of 60 wt% Al_2O_3 (Alcoa A16 SG, Alcoa, Ludwigshafen, Germany). Infiltration was performed at about 80 kPa air pressure to remove air bubbles which would otherwise remain trapped within the porous sample. The samples were dried at 60°C for 2 h, and then sintered for 1 h at 1300°C (1573 K) in flowing argon (2 litre h^{-1}) and 1 h at 1600°C (1873 K) in 1·5 MPa argon to obtain porous $SiC–Al_2O_3$ composites. The heating rate was 10 K min^{-1}.

The composite structure was investigated by light microscopy. The $SiC–SiO_2–Al_2O_3$ interface was examined by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and electron scanning microanalysis (ESMA).

3 RESULTS AND DISCUSSION

3.1 Pyrolysis of the polycarbosilane preform

The pyrolysis of the precursor mixture 'A' with 'B' in a two-step regime at 430°C and 650°C is a good means to prepare polycarbosilanes suited for slurry-infiltration. The open porosity of the pyrolyzed composite 'C' is about 50% and forms when pyrolytic gases leave the precursor mixture.

The composition of the unpyrolyzed SiC-precursors 'A' and 'B',[14] as determined by chemical analysis, and of the pyrolyzed precursors, as determined by thermal decomposition, is given in Table 1. The oxygen and nitrogen content of precursor 'A' is introduced by handling, storage and pyrolysis, and the oxygen and nitrogen contamination of precursor 'B' is introduced during pyrolysis.

The chemical reactions within both precursors during pyrolysis are described below,[7] however, pyrolysis was not performed at equilibrium conditions — due to the high heating rate, flowing argon atmosphere, and free evaporation of pyrolitic products — thus chemical processes cannot be quantified.

Precursor 'A' consists of poly(methylchloro) silanes and -carbosilanes with predominantly cyclic crosslinking.[7,8] The structure of the main components of 'A' is given in Fig. 1. After pyrolysis of 'A' at 650°C a weight loss of 20 wt% is observed. This weight loss evolves when hydrogen and hydrochloric acid (above 200°C), nitrogen and silanes with low molecular weight (above 300°C) and methane, nitrogen and carbon oxide (above 400°C) are released from the sample.[7,15] For example, atomic hydrogen and chlorine, which are bonded to either silicon or to the CH_2 side groups, are eliminated when thermal energy is supplied, and combine towards hydrochloric acid gas or molecular hydrogen. The polysilanes then further crosslink at the remaining reactive sites.[7] Note that the formation of amorphous SiC within pyrolyzed precursor 'A' will not occur below 800–1000°C.

Precursor 'B' is a crosslinked poly(phenylcarbosilane) with $[(Ph_2Si)_{1.5}SiPh(CH_2)_3]_x$ being the statistical composition, where Ph stands for one phenyl-group,[14] Fig. 1. During pyrolysis of 'B'

Table 1. Composition of pure precursors 'A' and 'B' before and after pyrolysis at 650°C or 1300°C (at%), total weight loss (wt%) and linear shrinkage (%)

	C	Si	H	Cl	N	O	Weight loss	Shrinkage
Precursor 'A'								
Unpyrolyzed	18	13	64	3	1	1	—	—
Pyrolyzed at 650°C	37	54	*	*	4	5	20	10
Pyrolyzed at 1300°C	42	48	—	—	4	6	28	25
Precursor 'B'								
Unpyrolyzed	49	5	46	—	—	—	—	—
Pyrolyzed at 650°C	Not determined						55	5
Pyrolyzed at 1300°C	77	18	—	—	1	4	60	25

*Hydrogen and chlorine were not determined by thermal analysis.

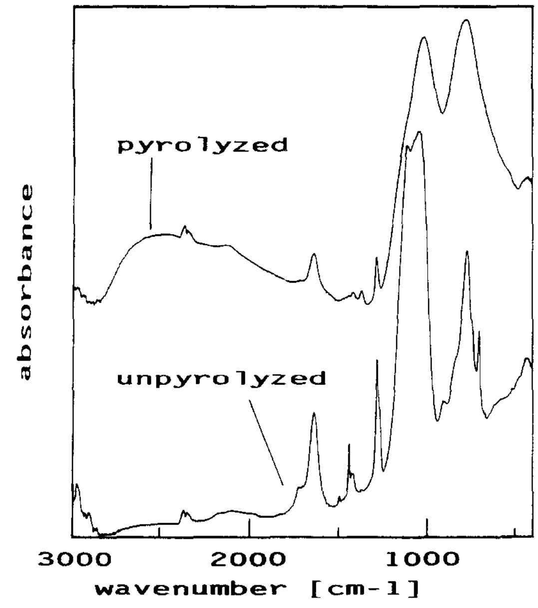

Fig. 2. IR-spectra of precursor mixture (75 wt% 'A' with 25 wt% 'B') before and after pyrolysis in flowing argon (2 litre h^{-1}) for 1 h at 430°C and for 2 h at 650°C.

hydrogen, benzene and probably di-phenylenes are released, leaving hereby reactive sites for further crosslinking. The weight loss of this precursor after pyrolysis at 650°C is 55%.

When the mixture of 'A' with 'B' is heated to 150°C, the polycarbosilane 'B' melts and acts as a binder between the particles of polysilane 'A'; these particles show some softening but no complete melting. Thus, the amount of 'B' necessary to provide complete bonding within the pyrolyzed mixture of 'A' and 'B' is determined by the particle size distribution of material 'A'. The mechanically ground particles of 'A' resemble flat shards, because synthesized 'A' has a foamy consistence. The particle size is between 20 and 400 μm, and the particle thickness varies between one tenth and one half of the particle size.

The precursors and their mixture were examined by infrared-spectroscopy before and after pyrolysis at 650°C. The spectra of mixture 'C' are dominated by the peaks of precursor 'A', as shown in Fig. 2. The characteristic peaks of precursor 'A' are between 1030 cm^{-1} and 1100 cm^{-1} (Si–CH_2–Si wagging), 1420 cm^{-1} and 1270 cm^{-1} (CH_2 deformation in Si–CH_3), at 2975 cm^{-1} (C–H stretching), 770 cm^{-1} (Si–C wagging) and between 1000 cm^{-1} and 1100 cm^{-1} (Si–O wagging).[7] Precursor 'B' has characteristic peaks, e.g. at 710 cm^{-1} and around 1050 cm^{-1}, due to skeletal vibrations and at 470 cm^{-1} due to a vibrational band of the Si–Si structure.[14] After pyrolysis of the precursor mixture at 650°C the intensity of the bands between 1030 cm^{-1} and 1100 cm^{-1} (Si–CH_2–Si wagging) and the bands at 1270 cm^{-1} and 1420 cm^{-1} (CH_2 deformation) was found significantly reduced (Fig. 2). Instead, the intensity of the band at 770 cm^{-1} due to vibrations of the Si–C bonds had clearly increased, indicating the formation of further polycarbosilanes within precursor 'A'.

Table 2. Composition of precursors 'A' and 'B' after pyrolysis at 1300°C, assuming that all oxygen and nitrogen exist as SiO_2 and Si_3N_4 (mol%)

	SiC	C	SiO_2	Si_3N_4
Precursor 'A'	91·3	—	6·5	2·2
Precursor 'B'	19·2	77·9	2·5	0·3

The significant differences in chemical composition, weight loss and shrinkage during pyrolysis between both precursors did not deter the formation of the composite polycarbosilane structure 'C', where pyrolyzed particles of 'A' are embedded in a matrix of pyrolyzed 'B' (Table 1). However, when pure uncoated samples of polycarbosilane 'C' were further pyrolyzed to nanocrystalline β-SiC[7] at 1300°C for 2 h, microcracks were observed between SiC derived from 'A' and 'B'. A comparison of the chemical composition of SiC derived from both precursors shows, that the differences in carbon, nitrogen and oxygen content should lead to distinct differences in the coefficients of thermal expansion of both SiC types, assuming that all oxygen exists as SiO_2 and all nitrogen exists as Si_3N_4 (Tables 2 and 3). Moreover, the distribution of oxygen and nitrogen within pyrolyzed precursor 'A' will differ locally and induce stresses within this SiC-type. The excess carbon of pyrolyzed precursor 'B' was found to be locally concentrated, because oxidized samples of this material showed small pores.[16] It is not clear whether this carbon distribution originates in diffusion processes during pyrolysis, or in unknown processes during the formation of the three-dimensional polycarbosilane network.

The heating cycle during pyrolysis of the precursor mixture and the composition of this mixture can be selected only within narrow limits. The pore structure of polycarbosilane 'C' will

Table 3. Coefficient of thermal expansion α (below 500°C) for some prospective components at the glassy reaction layer between SiC and Al_2O_3 ($\times 10^{-6}$ K^{-1})

Component	α
β-SiC	6
α-Al_2O_3	6·9
α-quartz	12·3
Mullite ($3Al_2O_3 \cdot 2SiO_2$)	4·5
SiO_2-glass	0·5
2 SiO_2–Al_2O_3 – glass*	1·5

*Calculated according to Ref. 20.

coarsen when the pyrolysis step at 430°C, which has the purpose of allowing pyrolytic gases to leave the sample, is omitted. When the second pyrolysis temperature is set higher than 650°C, the shrinkage of preform 'C' during later sintering at 1300°C will be less than 10%, and cracks will develop between SiC and the Al_2O_3 layer.

The ratio of the SiC-precursors 'A' and 'B' in the powdered mixture determines the mechanical stability of the porous polycarbosilane 'C' after pyrolysis at 650°C. A content of less than 20 wt% of meltable component 'B' is insufficient to provide stable incorporation of all the particles of material 'A'. A content of component 'B' of more than 30 wt% increases the median pore size by about 100% and isolated pores of 10^{-3} m diameter form. This coarsening of the pore structure is caused by the high amount of gases evaporating from component 'B' during pyrolysis at temperatures up to 430°C, where precursor 'B' is still pliable.

3.2 Sintering of the SiC–Al_2O_3 composites

The porous polycarbosilane preform 'C' was oxidized at 600°C to reduce the excess carbon of pyrolyzed precursor 'B' (in which pyrolyzed 'A' was embedded), and to provide wetting and bonding to the later applied Al_2O_3 layer. No weight change was observed after oxidation, as probably the weight loss by evaporation of carbon oxide was balanced by the weight gain due to oxidation. The sample surface then showed an oxygen-rich scale of less than 5 μm thickness.

During sintering of the Al_2O_3 slurry-coated samples 'C' at 1300°C, the pyrolysis of both precursors towards SiC was completed, mainly by further elimination of hydrogen and by significant structural changes. Above 800°C amorphous SiC forms and at 1000°C nanocrystalline β-SiC evolves.[7,14] After pyrolysis at 1300°C, the weight loss of pure 'A' increased to 28% and that of pure 'B' increased to 60%. The influence of the volatile pyrolytic products, such as hydrogen, on densification of SiC and Al_2O_3 during sintering at 1300°C is not clear, however, no detrimental effects were observed. After pyrolysis at 1300°C, the oxygen and nitrogen contents of precursor 'A' were unchanged (Table 1), indicating that the reactions between SiO_2 and the excess free carbon C, as described below, had not yet started. The composition of mixture 'C' after pyrolysis at 1300°C, as determined by thermal decomposition, coincided with that calculated from the composition of the individually pyrolyzed precursors. Apparently the pyrolytical processes within both precursors did not have enough influence on one another to induce changes in chemical composition.

When the sintering step at 1600°C was performed at normal pressure of argon, a weight reduction of 10–15 wt% was observed. Thus, the final sintering at 1600°C for densification of the Al_2O_3 layer was performed at 1·5 MPa argon to suppress chemical reactions between SiC, C and SiO_2, which would not only decrease the sample weight but also its density. The shrinkage of the Al_2O_3-coated preform 'C' during pyrolysis at 1300°C is 10%, and during sintering at 1600°C is about 5–8%. This shrinkage is again crucial for the crack-free densification of the Al_2O_3 layer and for its crack-free bonding to the oxidized SiC.

A reduction in the contents of oxygen and excess carbon has been reported for polycarbosilanes which were pyrolyzed at 1400°C.[17] For mixtures of SiC, SiO_2 and carbon, reaction schemes at temperatures above 1200°C have been described.[18,19] SiO_2 and C react towards SiO and CO; in a secondary reaction SiO reacts with C to SiC and CO;[18] in addition, SiC and SiO_2 may react to SiO and CO, as given below:[18]

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)}$$
$$SiO_{(g)} + 2\,C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)}$$
$$SiC_{(s)} + 2\,SiO_{2(s)} \rightarrow 3\,SiO_{(g)} + CO_{(g)}$$

After sintering at 1600°C in 1·5 MPa argon a weight loss of less than 3 wt% was obtained for the SiC–Al_2O_3 samples. Assuming that all oxygen exists as SiO_2 (Table 2), a theoretical weight loss of 9·5 wt% would be obtained for the SiC derived from precursor 'B' when its oxide and excess free carbon would react to silicon and carbon monoxide; the weight loss would be 7·4 wt%, if SiC was formed in a secondary reaction, as described above. However, the chemical reactions within the samples which lead to this weight loss cannot be described without an analysis of the volatile reaction products.

3.3 Characterization of the SiC–Al_2O_3 composite

The Al_2O_3 layer on the sintered porous SiC–Al_2O_3 samples was continuous and partially transparent. The density of the Al_2O_3 was 95% of theoretical density, as determined by scanning electron microcopy. The rims of the pores and pore channels of the composite were smooth and round, and the open porosity was 16–20%. Porosity was determined on photos of the composite, by measuring the area of the pores and of the solid. Pore size distribution was determined by measuring the diameters of 600 pores (Fig. 3). No cavities, where a flowing liquid would be trapped, were observed. The Al_2O_3 content of the sample was at least 40 wt%, and the

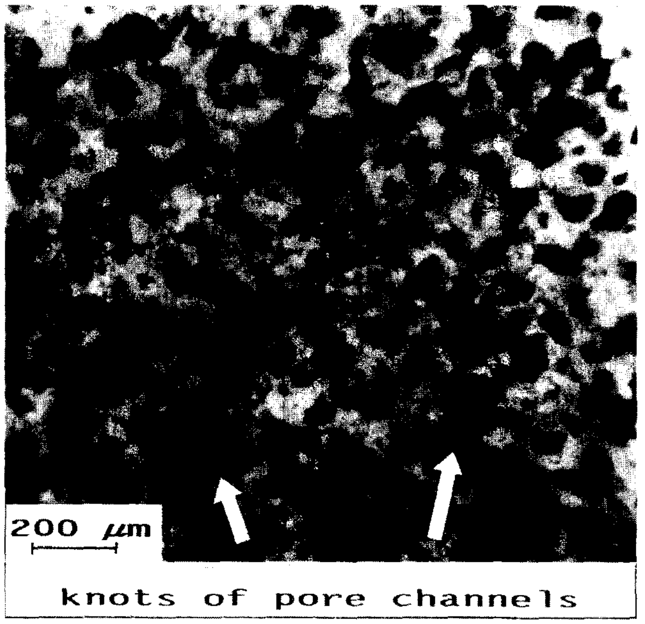

Fig. 3. Pore structure of the $SiC-Al_2O_3$ composite after final sintering for 1 h in 1·5 MPa argon at 1600°C.

SiC content was up to 60 wt%. So, with a porosity of 20%, the density of the composite samples will be about 2·8 g cm^{-3} (2·8 × 10^3 kg m^{-3}).

The pore size distribution was bell-shaped, and 92% of all pores were equal or smaller than 70 µm in diameter (Fig. 4). Pores with diameters between 80 µm and 110 µm were found at intersections of various pore channels. The few intersections (0·3% of all pores) which had a size of up to 200 µm, see arrows in Fig. 3, were omitted in the pore size distribution.

Between the SiC and the Al_2O_3 a probably 'glassy' layer had formed, its thickness was usually between 2 and 5 µm (Fig. 5). The width of this layer is predetermined by the surface oxidation of the pyrolyzed preform 'C', which proceeded irregularly as a result of the local deviations in composition. Occasionally, the thickness of the layer exceeded 10 µm, and then the layer seemed to spall off the SiC (Fig. 5).

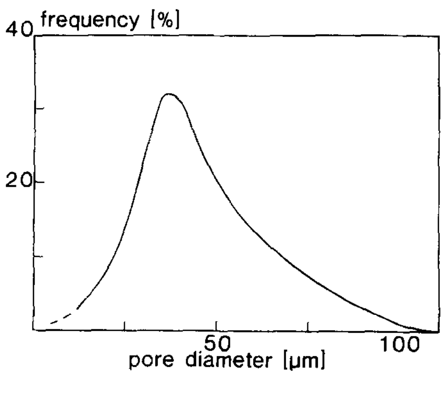

Fig. 4. Normalized pore size distribution of the $SiC-Al_2O_3$ composite; 7 300 pores per cm^2 (73 × 10^6 pores per m^2) with a diameter equal to or greater than 10 µm.

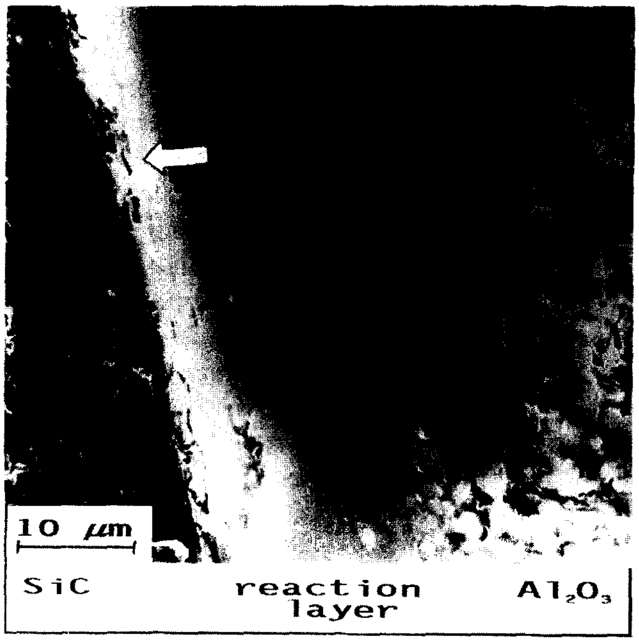

Fig. 5. SEM picture of the interface between SiC and Al_2O_3 after sintering at 1600°C; the arrow indicates microcracks.

The composition of the reaction layer varied gradually from SiO_2 near the SiC preform to predominantly Al_2O_3 at the surface of the Al_2O_3, as determined by energy dispersive X-ray analysis and by electron scanning microanalysis. At a distance of 20 µm from the glassy layer, the concentration of SiO_2 within the Al_2O_3 was still 5 at%, as determined by electron scanning microanalysis. Thus, the formation of the glassy layer with its composition gradient was the result of a combination of diffusion of SiO_2 into the Al_2O_3 and of glass forming reactions between SiO_2 and Al_2O_3. The diffusion probably proceeded along the grain boundaries, and occasionally, some isolated Al_2O_3 grains are found within the glassy layer (Fig. 5).

There are three locations for chemical reactions to take place within the porous $SiC-Al_2O_3$ composites during sintering at 1600°C. Reactions will occur within the SiC, between SiC, excess carbon and the SiO_2, as described in Section 3.2. At the interface between the SiC and its oxide scale, these two components might react to form gaseous SiO and CO. The third location for reactions is between the SiO_2 and the Al_2O_3, as these oxides form glasses at elevated temperatures. The thickness of this glassy zone probably increases during sintering, while Al_2O_3 grains are attacked by the melt. However, it is not clear whether or not these reactions interfere with each other, e.g. through gaseous products such as SiO and CO.

The coefficients of thermal expansion for some of the components which might be found at the glassy layer between SiC and Al_2O_3 are given in Table 3. Obviously elastic stresses exist along the glassy layer, which are responsible for the formation of microcracks whenever the thickness of the layer significantly exceeds 5 μm (Fig. 5).

Some experiments were performed with pyrolyzed preforms 'C' which had been oxidized only 5 min before slurry-dipping in order to determine the best oxidation conditions. These preforms showed incomplete wetting by the aqueous Al_2O_3 slurry. After sintering at 1600°C there was no continuous reaction layer between the SiC and the Al_2O_3. The formation of microcracks between SiC and Al_2O_3 due to incomplete wetting, and probably less due to elastic stresses, was observed. Thus, the oxidation of the polycarbosilane 'C' before its impregnation with the Al_2O_3 slurry is crucial to provide bonding between SiC and Al_2O_3. However the oxidation conditions have to be selected carefully to prevent the formation of microcracks along the interface between the reaction layer and the SiC.

4 CONCLUSIONS

Porous preforms, which consist predominantly of polycarbosilanes and which are suitable for slurry infiltration, are obtained by pyrolysis of a mixture of polysilanes and polycarbosilanes at 650°C. The porosity of these preforms is about 50%. An interpenetrating phase composite of $SiC–Al_2O_3$ can be prepared by oxidation of the pyrolyzed preform to promote wetting, subsequent infiltration with an aqueous Al_2O_3 slurry and pyrolysis and sintering in a two-step regime at 1300°C and 1600°C. The $SiC–Al_2O_3$ composite has an open porosity of up to 20%, and a bell-shaped pore size distribution, where 92% of all pores have a diameter smaller or equal to 70 μm.

Such macro-porous materials may have application as filters for liquids or as preforms for composite preparation by further infiltration processes.

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