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Polymer-Derived Si-Based Bulk Ceramics, Part I: Preparation, Processing and Properties

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Abstract

The synthesis and processing of dense silicon-based bulk ceramic materials derived from the thermal decomposition of preceramic organosilicon polymers such as polysilazanes and polysilanes was achieved by three different routes A, B, and C. Additive-free silicon carbonitride bodies of the composition $Si_{1.7}C_{1.0}N_{1.6}$ were produced according to route A, with up to 94% relative density by the pressureless pyrolysis of compacted infusible polysilazane powders at low processing temperatures (1000°C). The resulting silicon carbonitride was single-phase and amorphous according to X-ray- and TEM-investigations and exhibited a low solid-phase density of 2·33 g/cm³. The maximum room temperature fracture strength of additive-free silicon carbonitride was 370 MPa. Crystallization of the as-synthesized silicon carbonitride bulk samples occurred at temperatures exceeding 1400°C.

In a second process, route B, densification of polysilazane-derived amorphous silicon carbonitride powder was achieved by liquid phase sintering with alumina and yttria as sintering additives in nitrogen atmospheres and at temperatures up to 1900°C. This process resulted in the formation of dense polycrystalline β-Si_3N_4/β-SiC-composites. The average room temperature fracture strength and fracture toughness of the gas pressure sintered composite were in the range of 650 MPa and 10·2 MPa$\sqrt{m}$, respectively.

Polycrystalline Si_3N_4/SiC-composites were obtained in a third process, route C, by the pyrolysis and subsequent sintering of α-Si_3N_4-powder/polysilane blends. The Si_3N_4-powder serves as an inert filler reducing the volume shrinkage associated with the polymer-to-ceramic transformation. Dense Si_3N_4 and Si_2N_2O bulk ceramics were formed according to route B by the liquid phase sintering of amorphous silicon nitride powder synthesized by the polysilazane pyrolysis under ammonia.

1 Introduction

Advanced non-oxide Si-based materials such as Si_3N_4 or SiC are commonly produced by inorganic solid state reactions at high temperatures. Thus, SiC is synthesized by the reaction of silica with carbon according to the Acheson process at $T \geq 2000$°C. Silicon nitride is fabricated either by the reaction of the elements or by the nitridation of silica in the presence of carbon at $T = 1500$°C. Due to their predominantly covalent nature, high sintering temperatures in the range of 1700–2100°C and the addition of sintering aids have to be used to enhance the densification of compacts prepared from these materials. Since the work of Verbeek *et al.* and of Yajima *et al.* in the mid 1970's, it is known that these ceramics can be produced at unusually low temperatures, i.e. in the temperature regime of 800–1200°C, by the thermal decomposition of organosilicon preceramic polymers.[1,2] This process is known as preceramic polymer pyrolysis and involves the following reaction steps as demonstrated by Seyferth and Wiseman for the formation of Si_3N_4 or Si_3N_4/SiC-composites from polysilazanes.[3,4]

(1) Synthesis of Si-based oligomers or polymers from low molecular weight compounds:

$$RHSiCl_2 \xrightarrow{NH_3} [RHSiNH]_n + 2\ NH_4Cl \quad R = \text{alkyl}$$

(2) Enhanced chemical or thermal cross-linking of the as-synthesized polymers giving high

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molecular weight compounds suitable for polymer-to-ceramic transformation with high yields:

$$[RHSiNH]_n \xrightarrow{\text{strong base}} [RHSiNH]_{n-m}[RSiN]_m + m\ H_2$$

(3) Finally, pyrolysis of the cross-linked polymer providing the desired ceramic material:

$$[RHSiNH]_{n\ m}[RSiN]_m \xrightarrow{1000°C/Ar} Si_xC_yN_z + H_2 + RH$$

$$[RHSiNH]_{n\ m}[RSiN]_m \xrightarrow{1000°C/NH_3} Si_3N_4 + H_2 + RH$$

The preceramic polymer pyrolysis process has been intensively investigated with respect to the production of Si-based non-oxide fibers[2,5] and is already utilized commercially for the fabrication of SiC-, Si_3N_4-, and Si–C–N-fibers. Further potential applications such as infiltration of porous substrates, preparation of ceramic coatings, and joining of ceramics are under research.[6] However, the high potential of molecular preceramic compounds for the production of ceramic powders and bulk materials has been only sporadically demonstrated in the literature. Recently, great interest has been focussed on the *in situ* formation of β-Si_3N_4/β-SiC ceramic micro/nano-composites prepared by the densification of amorphous Si–C–N-powders at $T \gg 1000°C$.[7,8] The amorphous ceramic powders were produced either by the gas-phase decomposition of hexamethyldisilazane $((CH_3)_3Si)_2NH$[8] or by the solid-phase pyrolysis of poly(methyl)silazanes.[3,7,9] Hot-pressing of the Si–C–N-powders can result in β-Si_3N_4/β-SiC-composites which exhibit extraordinary high mechanical strength values ($\geq$1500 MPa)[8] or superplasticity at 1600°C.[10] According to a novel route, Si-containing polymers such as polysilazanes and polycarbosilanes can be processed directly to near dense monolithic ceramic bodies at low temperatures (1000°C) and without using additives by the thermolysis of inorganic polymer powder compacts.[11,12]

Besides the Si-based materials, other non-oxide ceramics such as AlN, BN, B_4C or TiN have also been synthesized by the pyrolysis of appropriate molecular compounds.[13,24] Some representative examples are listed in Table 1. In general, molecular compounds containing more or less direct polar bonds $M^{\delta+} - C^{\delta-}$ between the metal M and carbon are denoted as organometallics. In order to include for consideration the Si-containing polymers, the term organoelement polymer is used for the classification of materials such as polysilanes, polycarbosilanes, polysiloxanes, or polysilazanes.[25]

Generally, preceramic polymer pyrolysis is a process effective at relatively low temperatures and forming in many cases completely amorphous ceramic materials. Polymer-derived multi-component ceramic systems like Si–B–C–N start crystallizing at temperatures exceeding 1600°C, which makes the amorphous ceramics interesting materials for high temperature applications.[26] The controlled crystallization of the amorphous phases can itself be utilized for the synthesis of nano-structured ceramic monoliths or powders. However, the formation of ceramic bulk materials other than fibers starting from preceramic polymers is difficult owing to the fact that the release of the reaction gases formed during the thermolytic conversion of the polymer to the ceramic is associated with a high volume shrinkage, which can lead to crack formation. Furthermore, the use of meltable polymers can result in foaming and bloating of the material during the pyrolysis process. The present work has been undertaken to investigate the processing of organoelement compounds into dense bulk ceramics with the objective of avoiding these problems.

Table 1. A choice of preceramic molecular compounds for the synthesis of non-oxide ceramics

Preceramic molecular compound	*Ceramic product*	*Reference*
$[RAlNH]_n$	AlN	13
$[Cl_2Al\text{-}N(H)Si(CH_3)_3]_2$	AlN	14
$C_5H_5N \times BH_3$	BC_4N	15, 16
$HNC_4H_8NH \times BH_3$	BC_2N	17
$[HNBCl]_3 + ((CH_3)_3Si)_2NH$	BN	18
$H\text{-}[CH_3SiH]_n\text{-}H$	SiC	19
$[CH_3SiH\text{-}CH_2]_n$	SiC/C	2
$[((CH_3)_2Si)_x(CH_3SiC_6H_5)_y]_n$	SiC/C	20
$[CH_3SiHNH]_m\ [CH_3SiN]_n$	$Si_xC_yN_z$	3
$[(CH_3)_2SiO]_m\ [CH_3SiO_{1.5}]_n$	$Si_xC_yO_z$	21
$[B_{10}H_{12}H_2N\text{–}CH_2\text{–}CH_2\text{–}NH_2]_n$	B_4C/BN	22
$[(C_4H_9N)_2Ti]_n$	TiN	23
$Zr[BH_4]_4$	ZrB_2	24

In the present study, dichloro(diorgano)silanes of the general formula $RR'SiCl_2$ with R = H or CH_3 and R' = CH_3 or R = CH_3 and R' = C_6H_5 have been used as the starting materials for the synthesis of the silicon-based polymers and ceramic materials. Dichloro(diorgano)silanes are produced in large quantities by the Rochow synthesis[27] and are commonly used for the preparation of silicones which are produced on the order of 700,000 tons per year.

The organopolysilazanes of the form $[RR'SiNH]_n$ used in this work were synthesized by the reaction of chlorosilanes with ammonia and by subsequent cross-linking of the ammonolysis product with strong bases such as potassium hydride, KH, or with dichloromethylsilane, CH_3SiHCl_2.[3,28] Poly(organo)silanes were obtained by the Wurtz–Fittig analogous reaction of R_2SiCl_2 with Na/K alloys.[20,29] Pyrolysis and subsequent processing of the polysilazanes resulted in the formation of the ceramic materials $Si_xC_yN_z$ (silicon carbonitride),

Si_3N_4 or Si_2N_2O, whereas the thermal decomposition of the polysilanes provided SiC_{1+x}.

In Part I, we report on the synthesis of dense or near dense Si-based bulk ceramics other than fibers from the above organosilicon polymers. Some of the mechanical properties of the materials produced are discussed. In Part II, the polymer-derived bulk ceramic microstructures developed during thermolysis and sintering are investigated by analytical transmission electron microscopy.

2 Experimental

The preparation of various Si-based ceramic bulk materials starting from organoelement polymers was accomplished first by the direct pyrolysis of polymeric shapes (route A) and secondly by the pressureless sintering of polymer-derived amorphous ceramic powders with addition of sintering aids (route B). In a third process, route C, α–Si_3N_4-powder containing Al_2O_3 and Y_2O_3 as sintering additives was mixed with a SiC-forming precursor, pressed and finally sintered. The principal reaction paths used for the synthesis of the organosilicon polymers and the ceramic products derived therefrom are shown in Fig. 1. The different routes applied for the processing of the preceramic polymers to dense bulk ceramics are denoted as A, B, and C as illustrated in Fig. 2. Generally, synthesis and all manipulations of the organoelement polymers were done in glass vessels under Ar. The pyrolysis reactions were conducted in quartz tubes in flowing atmospheres (Ar (99·999% purity) or NH_3 (99·996% purity))[1] with heating rates of 0·5 to 5°C/min.

2.1 Characterization of the polymer-derived ceramics

The chemical analysis of the synthesized ceramic materials was performed by conventional analytical methods.[2]

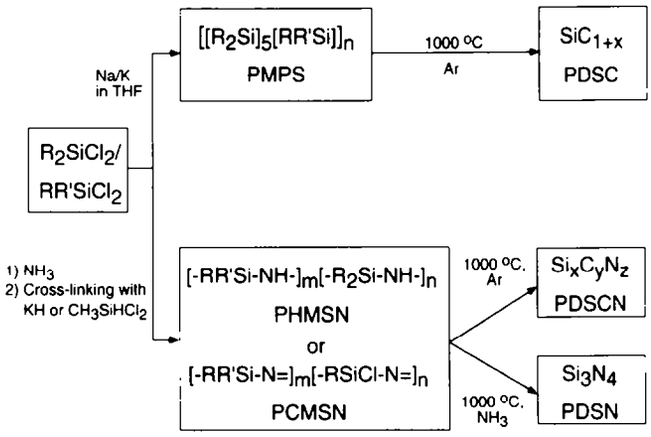

Fig. 1. Synthesis of Si-based polymers and the ceramic products obtained after pyrolysis in different atmospheres. R = CH_3, R' = H (reaction with NH_3) or C_6H_5 (reaction with Na/K); PMPS = poly(methylphenyl)silane; PHMSN = poly(hydridomethyl)-silazane; PCMSN = poly(chlorohydridomethyl)silazane; PDSC = polymer derived SiC; PDSCN = polymer derived silicon carbonitride; PDSN = polymer derived silicon nitride.

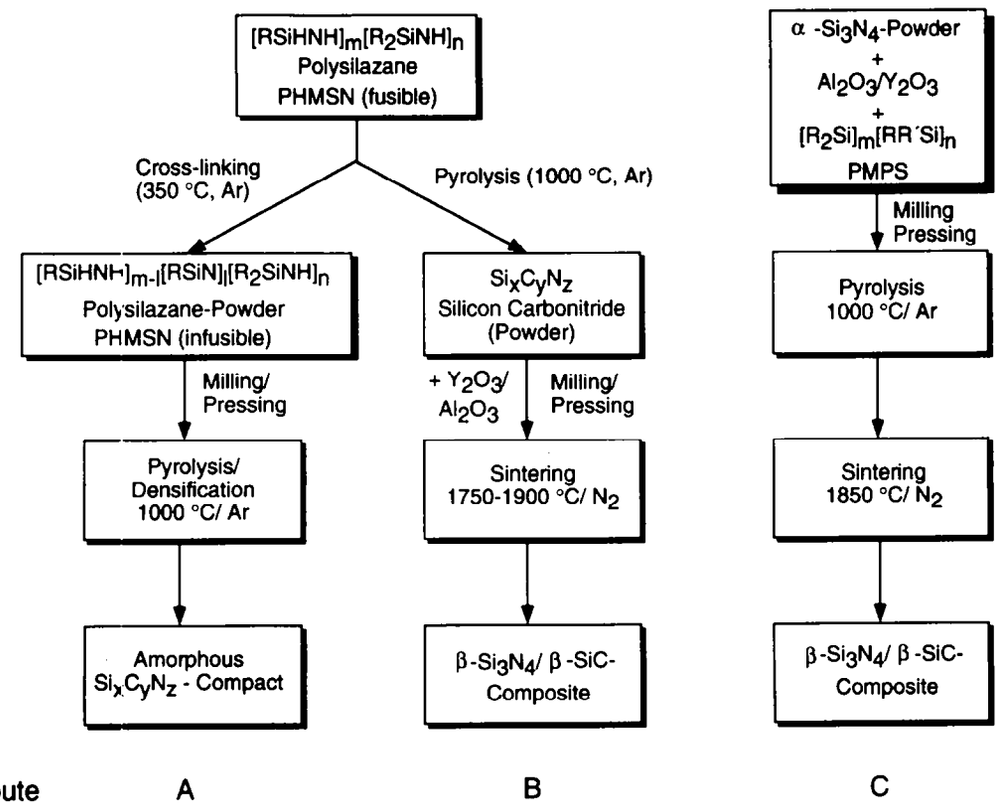

Fig. 2. Flow chart representing the processes A, B and C applied for the preparation of Si-based bulk ceramics derived from organoelement precursors. R = methyl (CH_3); R' = phenyl (C_6H_5H).

Phase compositions were determined by X-ray powder diffraction using monochromated CuK_α radiation (wavelength 154·178 pm).

For the determination of the ceramic solid-phase densities, the densified bulk samples were ball milled to powders. The solid-phase densities of the powders were then measured in a pycnometer using water as the liquid. Silicon carbonitride produced according to route A was analyzed in terms of BET surface area and pore size distribution by the measurement of the adsorption and desorption isotherms using N_2 or Ar as the adsorbing gas to ascertain the influence of possible nanoporosity on the solid-phase density. The solid-phase density of annealed and infusible polysilazane powder (PHMSN) was evaluated by pycnometry with n-hexane as the liquid. The bulk densities were determined by the water displacement method or, in the case of samples with open porosity, by mercury-pressure porosimetry. Relative densities were either based on theoretical densities calculated according to the rule of mixtures or on the ascertained solid-phase densities.

The amorphous silicon carbonitride was analysed by ESCA using Mg-K_α irradiation (1253·6 eV) as the X-ray source.[3] In order to avoid a charge shift due to the low electrical conductivity of the silicon carbonitride, the powder samples were mixed with Cu or Al powder (80 vol%) and uniaxially pressed to tablets.

Flexural strength was determined by the 4-point bend test[4] with an outer and inner span of 40 and 20 mm respectively in the case of room temperature testing and of 20 and 12 mm respectively in the high-temperature case. The flexural strength is given as the mean value calculated from eight specimens. Fracture toughness (K_{IC}) was evaluated by the indentation crack length method (ICL) according to Anstis *et al.*[30] The thermal decomposition of polysilazane-derived silicon oxynitride, Si_2N_2O, was investigated by TGA-MS.[5]

2.2 Synthesis and processing of the materials

2.2.1 Synthesis of additive-free monolithic silicon carbonitride (route A)

The starting material, poly(hydridomethyl)silazane (PHMSN) with the composition $[CH_3SiHNH]_m$ $[(CH_3)_2SiNH]_n$, was commercially available[6] and was used without purification.

In a typical experiment, 50 g of PHMSN were further cross-linked by thermally induced polycondensation for 100 min at 350°C in 0·1 MPa Ar and subsequently for 80 min in vacuum (2×10^{-3} Torr) at the same temperature. During the heat-treatment, a colourless liquid was distilled off and the overall mass loss was determined to be 12 wt%. The annealed PHMSN was infusible and insoluble in organic solvents such as toluene, THF or n-hexane. A solid-phase density of 1·22 g/cm^3 for the infusible polymer was evaluated. The polycondensation was investigated by simultaneous thermo-gravimetric and mass spectrometric (TGA–MS) measurements.[7] The material was then ball milled for 1 h with ZrO_2-balls, sieved through a 32 μm screen and finally compacted by cold isostatic pressing at 640 MPa into cylindrical samples 14 mm in diameter and in height or into rectangular bars having dimensions of 60 × 22 × 14 mm.[3] The relative green densities of the polymer green bodies were in the range of 84–89%. The main part of the pore volume exhibited pore radii of less than 100 nm, as determined by Hg-pressure porosimetry.[8] A minor amount of porosity with radii in the range of 10 μm was also detected. Subsequently, the polymeric green body was heated to 1000°C with a heating rate of 0·5–1°C/min in flowing Ar. Relative linear shrinkages of 25 up to 28% were detected and the overall yield of the black polymer-derived silicon carbonitride was found to be 68% relative to the PHMSN used. According to chemical analysis, the material contained 57·8 wt% Si, 14·3 wt% C, and 26·0 wt% N. From these values, an empirical formula $Si_{1·7}C_{1·0}N_{1·6}$ was derived for the synthesized silicon carbonitride (Table 2). The sample handled in air was contaminated with 0·8 wt% 0. Contamination of the ceramic residues with Zr stemming from the processing of the cross-linked polymer powder with ZrO_2 balls could not be detected. The as-pyrolyzed compacts exhibited relative bulk densities of 90–94% corresponding to a solid-phase density of 2·33 g/cm^3 and to open porosities in the range between 10 and 6% as found by Hg-pressure porosimetry (Table 3). The solid-phase density of PHMSN-derived silicon carbonitride (2·33 g/cm^3) deduced from Hg-pressure porosimetry was in good accordance with that determined by water

[1] Messer Griesheim, Germany.

[2] Optical emission spectrometry with inductively coupled plasma excitation (OES–ICP) was used for the determination of the Si-content; ICP 5500, Perkin Elmer, USA. Carbon and N were detected by carrier gas heat extraction (CGHE); equipment: C, S-analyser 244 and N, O-determinator TC 436, LECO Corp., USA.

[3] Modell ESCA 5300, Perkin Elmer Corp.

[4] Equipment: Zwick, Model 1474, Einsingen, FRG.

[5] Netzsch STA-QMS-system: 409/429-403, Selb, FRG.

[6] $[CH_3SiHNH]_m[(CH_3)SiNH]_n$ was obtained from the Nichimen Corporation, Tokyo, Japan, product name NCP200.

[7] TGA-STA 429, Netzsch Gerätebau, Selb, FRG, coupled with MS QMG 511, Balzers, Balzers, LIE.

[8] Hg-pressure porosimeter model 2000, Carlo Erba Instruments, Milan, Italy.

Table 2. Ceramic yields, elemental composition and solid phase densities of the synthesized organosilicon polymers PHMSN, PCMSN and PMPS (Fig. 1) pyrolysed under Ar and NH_3 without oxide additives

Preceramic organosilicon polymer	*Pyrolysis atmosphere/ temperature (°C)*	*Ceramic yield (wt%)*	*Composition (wt%)* Si	C	N	O	*Empirical Formula*[a]	*Solid phase density*[b] *(g/cm³)*
Cross-linked PHMSN	Ar/1000	68	57·8	14·3	26·0	0·8	$Si_{1.7}C_{1.0}N_{1.6}$	2·33
	NH_3/900	65	60·2	≤0·3	35·5	4·0	$Si_{3.4}N_4$	n.d.
PCMSN	Ar/1000	72	57·4	14·2	25·4	2·4	$Si_{1.7}C_{1.0}N_{1.5}$	2·30
	NH_3/1000	68	n.d.	≤0·5	35·2	3·1	$Si_{3.5}N_4$	n.d.
PMPS	Ar/1000	68	52·4	45·3	—	0·5	$SiC_{2.0}$	2·87[c]

[a]Molar composition neglecting the oxygen content.
[b]Water pycnometry of powdered bulk samples.
[c]Calculated according to the rule of mixtures assuming SiC and C as the phases formed during pyrolysis.

pycnometry of $Si_{1.7}C_{1.0}N_{1.6}$-powder (2·30 g/cm³). In addition, gas adsorption measurements of the as-synthesized silicon carbonitride powder revealed a BET surface area of 5·5 m^2g.Thus, it can be concluded that the pyrolysis of the polysilazane PHMSN gives fully dense amorphous silicon carbonitride powder particles without any detectable nanoporosity.

Pyrolysis of PHMSN-powder in NH_3 up to 900°C provided X-ray amorphous, white silicon nitride in 65% yield. The silicon content was measured to be 60·2 wt% (theoretical value for crystalline Si_3N_4: 60·0 wt%). Due to manipulation of the material in air, an oxygen contamination of 4 wt% was detected. The residual carbon content was below the detection limit of 0·3 wt%.

2.2.2 Synthesis and sintering of polysilazane derived Si-based ceramic powders with additives (route B)

Amorphous polysilazane-derived Si-based ceramic powders were obtained by the pyrolysis of poly(chlorohydridomethyl)silazane PCMSN in flowing Ar or in flowing NH_3. The synthesis of PCMSN is based on the reaction of oligomeric silazanes $[CH_3SiHNH]_n$ with dichlororganosilanes CH_3SiHCl_2[28] and is shown by the following simplified reaction equations:

$$RR'SiCl_2 \xrightarrow{NH_3} [-RR'Si-NH-]_n / R = H;\ R' = CH_3 \quad (1)$$

$$[-CH_3SiH-NH-]_x + yCH_3SiHCl_2 \xrightarrow[H_2/HCl]{30\text{–}300°C} [-CH_3SiH-N=]_m[-CH_3SiCl-N=]_n \quad (2)$$

Pyrolysis of PCMSN in argon at 1000°C gave a black X-ray amorphous silicon carbonitride powder with an empirical composition $Si_{1.7}C_{1.0}N_{1.5}$ and 72 wt% yield (Table 2). Decomposition of PCMSN in ammonia at 1000°C resulted in the formation of X-ray amorphous silicon nitride with 68 % yield. The nitrogen content was measured to be 35·2 wt%. The product was contaminated with 3·1 wt% oxygen and the residual carbon content was less than 0·5 wt%.

Prior to sintering, the different amorphous polymer-derived powders were attrition milled at 1000 rpm either in air or under Ar for 3 h after addition of Al_2O_3 and Y_2O_3 in various amounts. Isopropanol was used as the suspension medium and Si_3N_4-balls as the milling medium. After evaporation of the alcohol, the powder was sieved through a 160 μm-screen and subsequently cold-isostatically pressed at 640 MPa to form green compacts (cylinders 10 mm in length and 15 mm in diameter or rectangular strength-test bars 55 × 25 × 15 mm^3).

A graphite furnace[9] was used for the sintering experiments. Heating rates of 5 and 10°C/min were applied for all samples; the final temperatures were 1750 or 1850°C in 0·1 MPa nitrogen atmosphere.

Besides pressureless sintering of oxide-doped PCMSN-derived silicon carbonitride powder, post-gas-pressure sintering at 1900°C and 10 MPa N_2-pressure[10] was applied to yield polycrystalline Si_3N_4/SiC-composites.

2.2.3 Synthesis and sintering of α-Si_3N_4-powder/ 20 wt% PMPS-blends (route C)

The reaction of a mixture of 5 mol $(CH_3)_2SiCl_2$ and 1 mol $CH_3(C_6H_5)SiCl_2$[11] with Na/K-alloy in THF as the solvent provided poly(methylphenyl)-silane PMPS as shown in eqn 3.

$$5\ R_2SiCl_2 + RR'SiCl_2 \xrightarrow[-NaCl/KCl]{Na/K\text{–}alloy} [[R_2Si]_5[RR'Si]]_n \quad / R = CH_3;\ R' = C_6H_5 \quad (3)$$

Before the preparation of the ceramic-powder/ polymer-blends, as-synthesized PMPS was first heat-treated at 500°C for 5 h under Ar. The resulting product was an amber-coloured polysilane soluble in organic solvents and having a melting range of 100–120°C.

[9]Furnace GERO GmbH, Neuhausen, Germany.
[10]Furnace GERO GmbH, Neuhausen, Germany.
[11]The organochlorosilanes obtained from Merck, Darmstadt, Germany were used without further purification.

Attrition milled α-Si_3N_4-powder[12] containing 2·8 wt% AlN, 7·8 wt% Y_2O_3 and 1·4 wt% Al_2O_3 as sintering additives was mixed with 20 wt% annealed PMPS dissolved in THF. Subsequent evaporation of the solvent THF gave α-Si_3N_4-powder homogeneously coated with the polysilane PMPS. The α-Si_3N_4-powder/PMPS-blend was then cold-isostatically pressed at 640 MPa. Finally, pyrolysis and sintering of the cold-isostatically pressed polymer-powder mixture was conducted under 0·1 MPa Ar at temperatures up to 1000°C in a quartz tube and under 0·1 MPa N_2 up to the final sintering temperature of 1850°C in a graphite furnace.[8]

3 Results and discussion

3.1 Synthesis and processing of the materials

The chlorosilanes were reacted either with Na/K-alloy or with NH_3 providing various types of organoelement ceramic precursors (Fig. 1). Basically, polymers with a high viscosity and a low volatility have to be synthesized to produce dense bulk ceramic materials. Best results, i.e. the highest ceramic yields, are obtained using infusible polymers.[13]

The following different polymer processing routes (A, B, and C) were used to produce dense or near dense bulk ceramics (Fig. 2).

Route A in Figure 2

During the proceeding polycondensation of fusible PHMSN at 350°C, mainly ammonia and hydrogen were evolved as could be determined by simultaneous thermal gravimetric and mass spectrometric (TGA–MS) investigations. The evolution of H_2 indicates that the thermal cross-linking proceeds via the formation of three-dimensional bridging [RSiN]-units:

$$[RSiHNH]_m[R_2SiNH]_n \xrightarrow{350°C/-H_2} \begin{matrix}[RSiHNH]_{m-l}[RSiN]_l \\ [R_2SiNH]_n\end{matrix} \quad (4)$$

Ammonia is formed during the heat-treatment due to condensation of H_2N-polymer end groups. An infusible polysilazane PHMSN was isolated as the reaction product (Fig. 2). The subsequent thermolysis of the compacted infusible polysilazane powder at 1000°C in Ar gave amorphous, additive-free silicon carbonitride compacts with dimensions of 42 × 16 × 10 mm^3. According to our studies, the crack-free polymer to ceramic transformation process succeeds if the following requirements are met:

- The organoelement polymer has to be infusible to enable the compact to shrink while retaining its shape during the heat-treatment.
- After shaping of the polymer-powder, a transient open porosity has to be present to allow the volatile reaction gases to be released without forming cracks and gas bubbles.
- Finally, during ceramisation, the original polymer particles have to form a continuous three-dimensional network by the formation of new covalent bonds between the individual polysilazane powder particles.

Route B in Figure 2

The infusible polysilazane powder was first pyrolyzed in Ar to an amorphous Si–C–N ceramic powder and then processed into dense polycrystalline β-Si_3N_4/β-SiC-composite ceramics by liquid phase sintering at higher temperatures (Fig. 2). Using ammonia instead of Ar during pyrolysis of the polysilazane powders PHMSN and PCMSN results in the formation of X-ray amorphous Si_3N_4-powder (Fig. 1). During attrition milling in wet isopropanol, the reactive amorphous Si_3N_4-powder takes up oxygen by hydrolysis or by alcoholysis in such amounts that pure polycrystalline silicon oxynitride, Si_2N_2O, is formed after densification at 1600°C in 0·1 MPa N_2 when Al_2O_3 and Y_2O_3 were added to this powder. Accordingly, the oxygen content increased from 3·1 wt% in the as-pyrolyzed (NH_3) material to 14·8 wt% in the attrition milled powder. The oxygen content of crystalline Si_2N_2O is calculated to be 14·0 wt%. The oxygen contamination can be reduced to 6·7 wt% by the use of dried isopropanol as the suspension medium and by attrition milling under an Ar atmosphere. In contrast, the oxygen content of the carbon containing silicon carbonitride powder attrition milled in wet isopropanol in air was significantly lower (4 wt%) owing to a strongly decreasing sensitivity of these powders towards moisture.

Route C in Figure 2

Pyrolysis of polysilane PMPS in Ar at 1000°C resulted in the formation of X-ray amorphous SiC_{1+x} with $x = 1$[29] (Fig. 1). In the present investigation, we used PMPS for the *in situ* formation of inter- and intragranular SiC dispersions in a Si_3N_4 matrix.

The ceramic yields, elemental composition and solid-phase densities of the pure organosilicon polymer-derived ceramics are listed in Table 2. Details of the processing of the polymers to dense bulk ceramics and some characteristic data of the densified products such as density, porosity and phase composition are summarized in Table 3.

[12]LC 12 H.C. Starck, Germany.

[13]In contrast, meltable and soluble polymers with lower viscosities are suitable for infiltration processes, for fiber preparation, and for the formation of coatings.

Table 3. Preparation of polymer-derived Si-based bulk ceramics according to the routes A, B, and C in Fig. 2, its final densities and compositions

Processing conditions	*Final ceramic material*			
	$Si_xC_yN_z$	*β-Si_3N_4/β-SiC*	*β-Si_3N_4/β-SiC*	*Si_2N_2O*
Route (see Fig. 2)	A	B	C	B
Starting Materials	PHMSN	PCMSN	α-Si_3N_4-powder +20 wt% PMPS	PCMSN
Additives (wt%) (Al_2O_3/Y_2O_3)	-	15[a]	12[b]	15[a]
Pyrolysis-Temperature (°C)	1000/Ar	1000/Ar	1000/Ar	1000/NH_3
	Sintering conditions and properties			
Temperature (°C)[c]	1000/Ar	1850/N_2	1850/N_2	1600/N_2
Solid phase density (g/cm³)	2·33	3·32	3·33	2·84
Bulk density (g/cm³)	2·15–2·01	3·25	3·22	2·81
Open porosity (%)	6–10	—	—	—
Matrix-composition	$Si_{1.7}C_{1.0}N_{1.6}$[d]	β-Si_3N_4/24 wt% β-SiC	β-Si_3N_4/10 wt% β-SiC	Si_2N_2O

[a] 10 wt% Y_2O_3 and 5 wt% Al_2O_3.
[b] 2·8 wt% AlN, 7·8 wt% Y_2O_3 and 1·4 wt% Al_2O_3.
[c] 1 h isothermal hold at the final temperature. Sintering was conducted at 0·1 MPa gas pressure.
[d] The silicon carbonitride is amorphous according to X-ray and TEM investigations.

3.2 Characterization of the polymer-derived ceramics

3.2.1 PHMSN-derived monolithic silicon carbonitride (route A)

Generally, the volume shrinkage caused by the thermal decomposition of a polymeric compound (*P*) into a ceramic (*C*) with the simultaneous formation of gaseous reaction products (*R*) according to eqn (5)

$$P_{(s,l)} \rightarrow C_{(s)} + R_{(g)} \tag{5}$$

depends on the change in the density of the contributing phases and on the ceramic yield α (≤ 1). The yield α is defined as the ratio of the mass of the polymer-derived ceramic (M_C) to that of the applied polymer (M_P):

$$\alpha = \frac{M_C}{M_P} \tag{6}$$

The overall change in the volume (ΔV) can then be expressed in terms of the mass (M) and solid-phase density (D) of the condensed phases considered in eqn (5):

$$\Delta V = \frac{M_P(D_C - \alpha D_P)}{D_P D_C} \tag{7}$$

or:

$$\Delta V\,[\%] = \frac{D_C - \alpha D_P}{D_C} 100 \tag{8}$$

The polymer to ceramic transformation of shaped PHMSN bodies according to route A in Fig. 2 provided silicon carbonitride compacts with up to 94% rel. density and with the composition $Si_{1.7}C_{1.0}N_{1.6}$. In this case, the densities D_P, D_C, and the ceramic yield α were determined to be 1·22 g/cm³, 2·33 g/cm³, and 77%. From this, the calculated value ΔV of 59·7, however, is about 5% lower than the experimentally determined relative volume shrinkage of 65%. This finding suggests that additional densification processes occur during pyrolysis that enable the porous polymeric body to form dense ceramic materials, even at these low reaction temperatures (800–1200°C).

The SEM micrograph of a polished surface of PHMSN-derived silicon carbonitride bulk sample is shown in Fig. 3. It is evident that pore sizes up to 10–15 μm are present which is in accordance with the pore size distribution measurements from Hg pressure porosimetry.

In order to evaluate the microstructural features of amorphous silicon carbonitride, $Si_{1.7}C_{1.0}N_{1.6}$ obtained after pyrolysis of PHMSN at 1000°C in Ar, ESCA and analytical TEM investigations were performed. The ESCA results support a single phase amorphous material. The ESCA Si(2p)

Fig. 3. SEM micrograph of a polished surface of PHMSN-derived silicon carbonitride bulk material prepared according to route A.

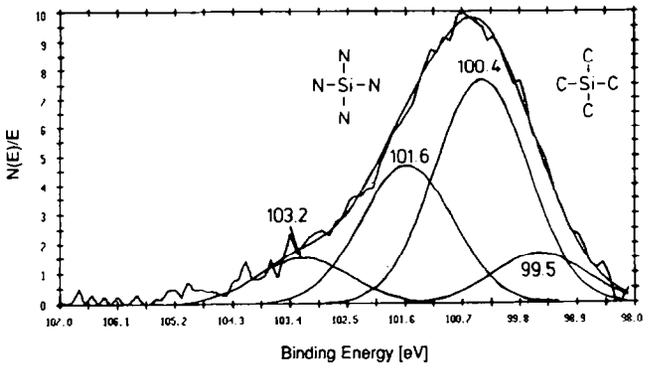

Fig. 4. ESCA Si(2p) spectrum of PHMSN-derived amorphous silicon carbonitride.

spectrum has to be deconvoluted using at least four Gaussian functions as shown in Fig. 4 indicating the presence of Si–N and Si–C bonds in the polysilazane derived material. The bonding energy at 99·5 and at 101·6 eV are associated with SiC_4- and SiN_4-units, respectively, whereas that at 100·4 eV is due to $SiN_{4-x}C_x$-units. The bonding energy located at 103·2 eV is related to the presence of oxygen contamination in the form of silica or silicon oxynitrides. Additionally, no SiC-shoulder can be assigned in the ESCA Si(2p) spectrum in contrast to reports for a mechanical Si_3N_4/SiC mixture.[31] The measured binding energy curve of the N(1s) electron can be deconvoluted into at least two Gaussian peaks with maxima located at 397·4 eV and 398·6 eV corresponding to N–Si and N–C bonds, respectively. The deconvoluted C(1s) peaks clearly indicate the presence of C–C (284·2 eV), C–N (286·4 eV), and Si–C bonds (282·7 eV).

Analytical TEM investigations revealed that the pure silicon carbonitride is completely amorphous and a single phase material. No segregations of C, SiC or Si_3N_4 could be found by the evaluation of the microstructure by means of electron spectroscopic imaging (ESI) in an energy filtering TEM.[32] Even after long annealing times in the order of 50 h under 0·1 MPa N_2 at 1000°C, the material remained amorphous without any phase partitioning. Accordingly, the synthesized silicon carbonitride can be considered as a metastable solid solution. It is worth to mention that such a material cannot be produced by conventional synthesis, i.e. by mixing and heat-treating of SiC and/or C with Si_3N_4.

The determined solid-phase density D_C = 2·33 g/cm^3 of the silicon carbonitride is significantly lower than that of the thermodynamically stable phases of $Si_3N_4$and SiC ($\rho \sim 3{\cdot}2$ g/cm^3). According to the rule of mixtures, solid-phase densities between 2·97 and 3·14 g/cm^3 were expected if the sample is considered to contain amorphous and/or crystalline Si_3N_4, SiC and C (graphite). The low density cannot be explained by nanoporosity since gas adsorption measurements clearly indicated the formation of fully dense silicon carbonitride powder. This phenomenon is associated with a highly disordered solid-phase structure and is in part caused by residual Si–H and C–H bonds which are still present in the material pyrolyzed at 1150°C in Ar as determined by infra-red investigations. In the infra-red spectrum, silicon carbonitride reveals broad vibration bands located at 1250–720 cm^{-1} and 600–415 cm^{-1} indicating the presence of Si–N- and Si–C-bonds. In addition, sharp absorption bands located at 2950–2850 cm^{-1} and at 2164 cm^{-1} are due to aliphatic C–H- and Si–H bonds. The relative openness of amorphous SiC-based ceramics prepared by polymer pyrolysis has also been reported by Soraru *et al.*[33] The solid-phase density of the silicon carbonitride increased from 2·33 g/cm^3 at 1000°C to 2·40 g/cm^3 at 1400°C and is related to the successive loss of residual hydrogen.

The Vickers Hardness, HV, of silicon carbonitride synthesized at 1150°C was determined to be 10 GPa in a sample with 6% open porosity. The median value of the fracture strength σ_B is of the order of 170 MPa with a maximum value of 370 MPa.

Crystallization of $Si_{1{\cdot}7}C_{1{\cdot}0}N_{1{\cdot}6}$ started at temperatures exceeding 1400°C and gave α-Si_3N_4 and α/β-SiC. In contrast, amorphous Si_3N_4 obtained by the mineralization of PHMSN under NH_3 was completely crystallized to α-Si_3N_4 at 1200°C and 30 min soaking time. This behavior reveals a significantly higher thermal stability of the compositionally more complex ternary system Si–C–N. The high thermal stability of precursor-derived Si–C–N ceramics was also observed by D. Mocaer *et al.*[34] The crystallization was accompanied by a weight loss reaching 10·3% after 50 h annealing of the silicon carbonitride bulk material at 1600°C in nitrogen and is associated with the solid state reaction of carbon with silicon nitride partitioned during the course of heat-treatment. Thermodynamically, the excess carbon reacts at temperatures exceeding 1440°C with the Si_3N_4-particles under 0·1 MPa nitrogen pressure according to the following reaction:[35]

$$Si_3N_4 + 3C \rightarrow 3SiC + 2N_2 \qquad (9)$$

3.2.2 PCMSN-derived β-Si_3N_4/24 wt% β-SiC-composites and Si_3N_4-ceramics (route B)

Silicon carbonitride powder with the composition $Si_{1{\cdot}7}C_{1{\cdot}0}N_{1{\cdot}5}$ derived from PCMSN was liquid phase sintered according to route B (Fig. 2, Table 3) with Al_2O_3 and Y_2O_3 (weight ratio = 1 : 2) as sintering aids and at 0·1 MPa N_2-pressure resulting in the in situ formation of β-Si_3N_4 and β-SiC polycrystals as the matrix phase. During the course of densification, β-Si_3N_4- and Si_2N_2O-particles crystallized first as could be determined by

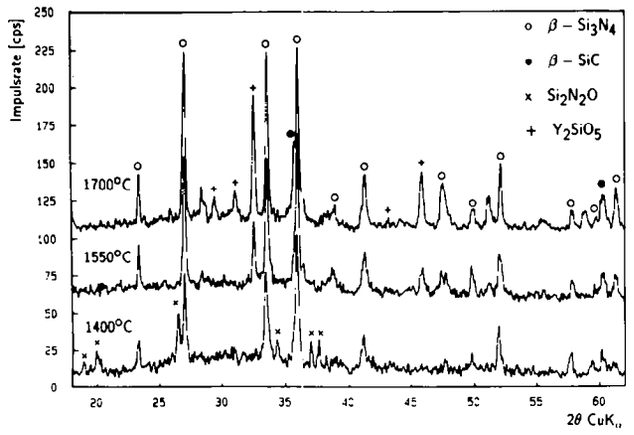

Fig. 5. X-ray diffractograms of cold-isostatically pressed PDSCN powder heat-treated at various temperatures in N_2 without isothermal hold in the presence of 10 wt% Y_2O_3 and 5 wt% Al_2O_3 according to process B.

sintering the cold-isostatically pressed silicon carbonitride powder samples without any holding time at various temperatures. The X-ray diffractograms shown in Fig. 5 clearly show that β-SiC begins to crystallize at temperatures above 1500°C, whereas β-Si_3N_4 is identified at $T \leq 1400$°C. The intermediate generation of silicon oxynitride Si_2N_2O evident at 1400°C cannot be observed at higher temperatures. Crystallization of a part of the amorphous oxide phase in the form of Y_2SiO_5 was also observed in the material annealed at $T \geq 1550$°C. The sintering of the amorphous Si-, C-, and N-containing starting powder has been proposed to proceed via a particle disintegration mechanism.[7] These findings are in accordance with the TEM studies of the microstructure developed at different final temperatures during liquid phase sintering of silicon carbonitride powder.[32]

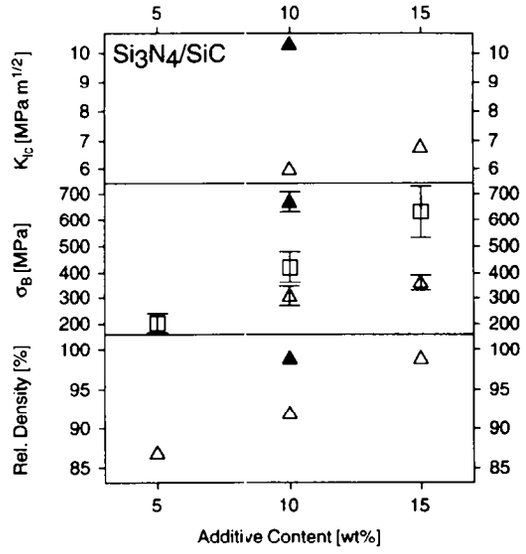

Fig. 6. Sintering densities, fracture strength and toughness (average values) of PCMSN-derived Si_3N_4/SiC-composite versus additive content (Y_2O_3/Al_2O_3 = 2:1). Δ = samples liquid phase sintered at 1850°C and 0·1 MPa N_2-pressure for 1 h according to process B; the filled triangles represent the values of samples which have been subsequently gas-pressure sintered at 1900°C and 10 MPa N_2-pressure for 1 h; □ = fracture strength values measured at 1000°C in air.

In Fig. 6, relative densities and some mechanical properties of the densified samples are shown as a function of additive content. The highest relative density was obtained by the addition of 15 wt% oxides. In the case of 10 wt% sintering aids, similar high densities were measured after gas-pressure sintering of presintered samples. The flexural strength significantly increased from 320 MPa at room temperature to 635 MPa at 1000°C. A maximum value of 700 MPa was attained. This phenomenon may be associated either with the reduction of internal stresses at elevated temperatures or with the reduction of surface defects owing to crack blunting via oxidation during the measurements in air. At temperatures exceeding 1100°C, the strength value strongly decreased due to the beginning of softening of the glassy phase. The room-temperature strength was improved from 280 to 650 MPa for the gas pressure sintered sample. The K_{IC} value was determined to be 10·2 MPa$\sqrt{m}$ which is nearly twice the fracture toughness measured in the presintered material (5·8 MPa$\sqrt{m}$). In Fig. 7, the resulting microstructure and the crack path induced by a Vickers indenter are shown. Due to gas-pressure sintering at a relatively high temperature (1900°C) large rod-like grain sizes up to 40 μm in length were found in

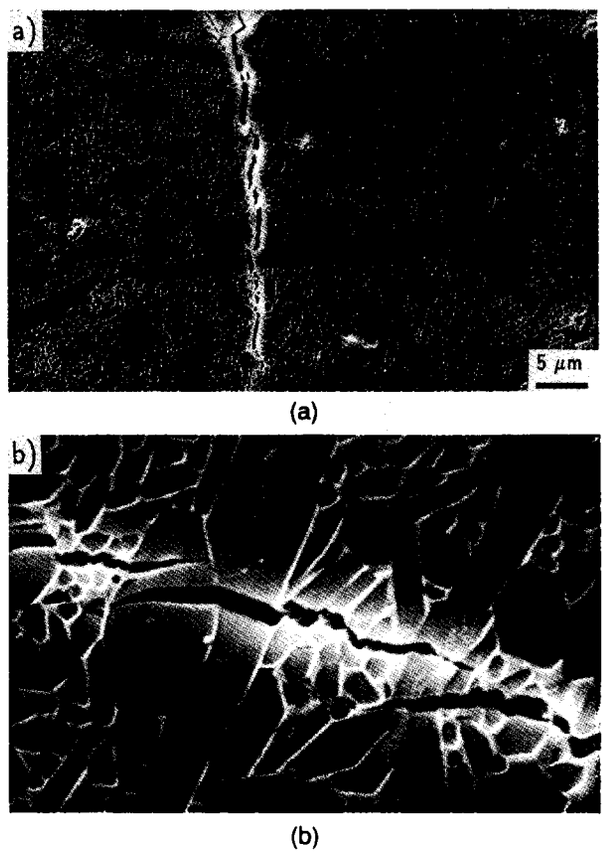

Fig. 7. (a) SEM micrograph of the microstructure of gas pressure and liquid phase sintered β-Si_3N_4/β-SiC composite according to route B (polished and plasma etched surface). The crack has been induced by a Vickers indenter. The micrograph (b) shows a section at higher magnification indicating the occurrence of crack branching. For sintering conditions see Fig. 6.

the β-Si_3N_4/β-SiC microstructure. The rod-like growth is typical for β-Si_3N_4 sintered with 15 wt% additives in the weight ratio Y_2O_3/Al_2O_3 = 2:1.[36] Besides these large, elongated particles, small crystallites in the range of 0·5 μm to several microns were also present.

The crack path induced by a Vickers indenter in the gas pressure sintered sample exhibited both intergranular and transgranular fracture modes as can be seen in Fig. 7. In addition, the crack path reveals the presence of crack branching (Fig. 7(b)) and indicates microcracking causing the relatively high fracture toughness measured. The distance between two crack branches is estimated to be about 5 μm. It is evident that the cracks always stop in a region consisting of small grains as can be also seen in Fig. 7(b). Further investigations on the toughening mechanism operating in the polymer-derived Si_3N_4/SiC-composites are in progress.

The ammonolysis of PCMSN at 1000°C resulted in the formation of amorphous silicon nitride (Fig. 1). Densification of the PCMSN-derived amorphous Si_3N_4-powder (PDSN) containing yttria and alumina as the sintering aids gave dense polycrystalline Si_3N_4-ceramics. X-ray diffraction patterns of the densified samples revealed the presence of the β-modification of Si_3N_4 exclusively. The final densities and mechanical properties vs. the additive content of the sintered PDSN-powder are given in Fig. 8. Figure 9 shows a typical microstructure of the sample densified at 1750°C containing 15 wt% additives. A crack path induced by a Vickers indenter reveals predominant intergranular fracture mode as is represented in Figure 9(b).

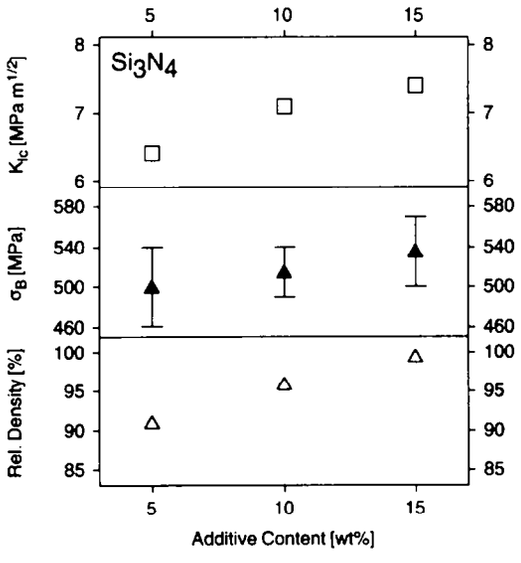

Fig. 8. Mean values of sintering densities, fracture strength and toughness of PCMSN-derived Si_3N_4-ceramic versus additive content (Y_2O_3/Al_2O_3 = 2:1). Sintering was conducted according to process B at 1750°C for 1 h under 0·1 MPa N_2.

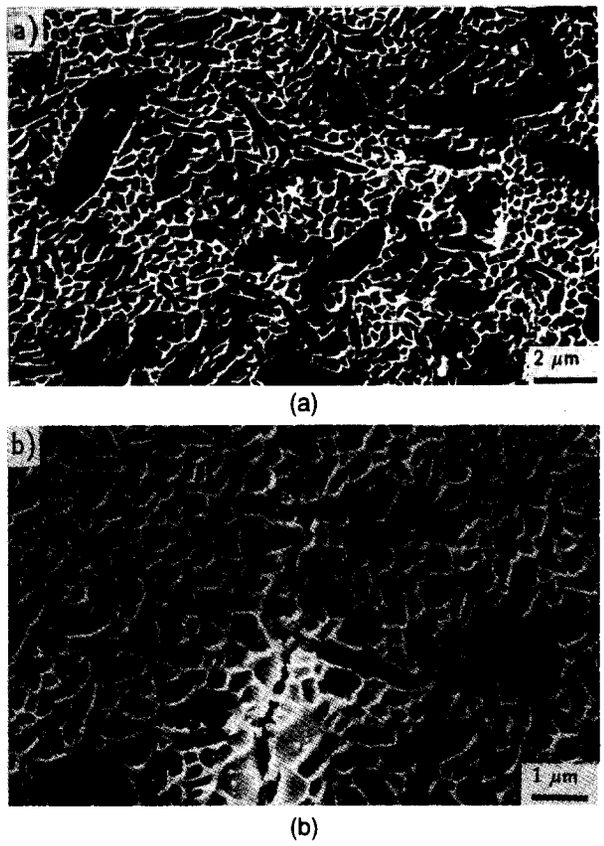

Fig. 9. (a) SEM micrograph of a polished and plasma etched section of the PCMSN derived Si_3N_4 microstructure. The micrograph (b) shows the fracture path induced by a Vickers indenter. The sample was liquid phase sintered after route B at 1750°C for 1 h and 0·1 MPa N_2 pressure with 10 wt% Y_2O_3 and 5 wt% Al_2O_3 as sintering additives.

3.2.3 PCMSN-derived Si_2N_2O (route B)

Besides SiC and Si_3N_4, Si_2N_2O is a potential material appropriate for high-temperature engineering applications. Thermodynamic calculations indicate a superior stability in oxidizing environments,[37,38] compared to Si_3N_4 and SiC. Generally, the pressureless densification of Si_2N_2O-powders is difficult due to its decomposition[39] at temperatures above 1580°C according to eqn (10)

$$3Si_2N_2O \rightarrow 3SiO + Si_3N_4 + N_2 \qquad (10)$$

Therefore, Si_2N_2O-materials with relative densities higher than 95% can only be obtained by hot or hot isostatic pressing of Si_3N_4 and SiO_2 powders at temperatures greater than 1800°C.[38] The use of double oxide sintering aids such as a combination of Al_2O_3 with Y_2O_3 lowers the eutectic temperature and ensures liquid phase sintering yielding final relative densities up to 93%.[39]

We found that PCMSN-derived amorphous silicon oxynitride can be densified at 1600°C in 0·1 MPa nitrogen atmosphere up to 97 and 99% of relative density in the presence of 10 and 15 wt% oxide additives (Figs 10 and 11), respectively. According to X-ray diffraction analysis of the

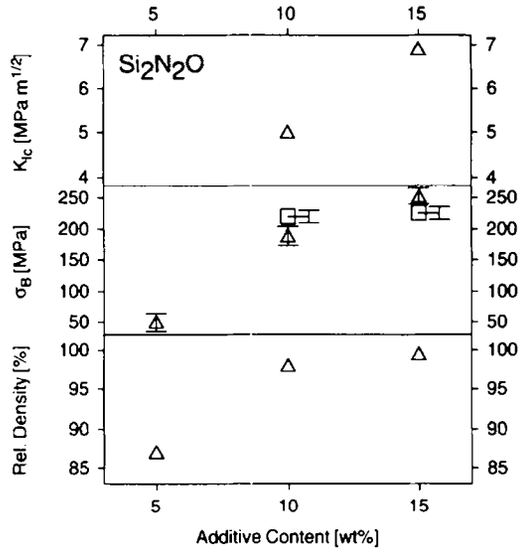

Fig. 10. Average values of sintering densities, fracture strength and toughness of PCMSN-derived Si_2N_2O-ceramic versus additive content (Y_2O_3/Al_2O_3 = 2:1) prepared after process B. Δ = samples sintered at 1600°C for 1 h and 0·1 MPa N_2-pressure; □ = fracture strength values measured at 1000°C in air.

densified sample, the amorphous powder crystallizes to Si_2N_2O, exclusively. No diffraction lines due to silicon nitride polymorphs, indicating the decomposition of the oxynitride phase, could be detected up to 1600°C (Fig. 12). At higher temperatures, β-Si_3N_4 is generated as the crystalline phase. Thermal gravimetric investigations in combination with a mass spectrometer (TGA–MS) of amorphous Si_2N_2O under 0·1 MPa He pressure revealed that the evolution of SiO with m/e = 44 was already detected in small amounts at $T \geq 1400$°C indicating the starting decomposition of the material. Owing to the reduced nitrogen pressure under these conditions, the decomposition of Si_2N_2O occurred at lower temperatures.

The diagrams depicted in Fig. 10 show the relative densities, the mechanical strength, and the K_{IC}

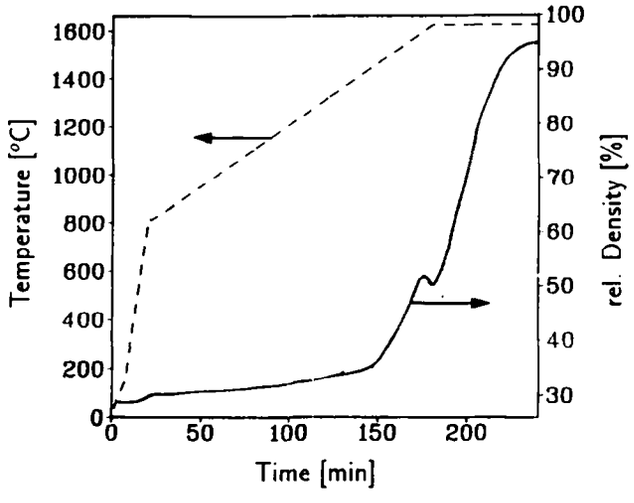

Fig. 11. Density and temperature versus time during sintering according to route B under 0·1 MPa N_2 of PCMSN derived amorphous Si_2N_2O-powder. 10 wt% Y_2O_3 and 5 wt% Al_2O_3 have been used as sintering additives.

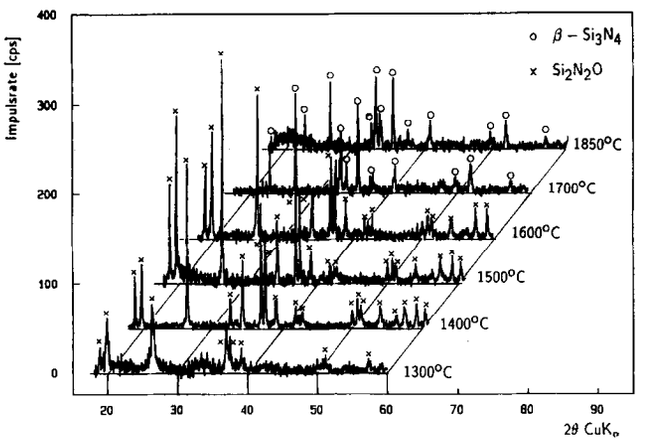

Fig. 12. X-ray diffractogramms of amorphous Si_2N_2O heat-treated for 15 min at various temperatures in the presence of 6·66 wt% Y_2O_3 and 3·33 wt% Al_2O_3 under 0·1 MPa N_2.

values of the sintered Si_2N_2O-material versus the amount of sintering aids. Depending on the final density, the mechanical strength values at room temperature are in the range of 205 (ρ = 97%, 10 wt% additives) and 230 MPa (ρ = 99%, 15 wt% additives) and are retained up to 1000°C. At higher temperatures, the fracture strength rapidly decreases.

3.2.4 α-Si_3N_4-powder/20 wt% PMPS-blend (route C)
The high linear shrinkage of up to 28% found during polymer to ceramic transformation of compacted polysilazane powders (route A in Fig. 2) can be significantly reduced by mixing the polymeric fraction with inreactive powders. Thus a α-Si_3N_4-powder/20 wt% PMPS-mixture prepared according to route C in Fig. 2 and pyrolysed at 1000°C in Ar showed a linear shrinkage of up to 3–4%. The sintered composite sample contained 10 wt% SiC in situ generated from the polysilane PMPS used as determined by chemical analysis (Table 2).

According to TEM studies, the resulting microstructure of the liquid phase sintered samples revealed the presence of SiC crystallites with grain sizes in the range between 20 and 200 nm embedded either intra- or intergranular in the Si_3N_4 matrix; the structure is described in detail in Part II.[32]

Pyrolysis of pure PMPS at 1000°C in Ar without Si_3N_4-powder and without additives gave a ceramic with a molar composition $SiC_{2.0}$. Crystallization started at $T \geq 1200$°C forming nano-sized β-SiC as the crystalline phase.[40] The median crystallite size was derived from the line broadening of the SiC(100)-reflexions in the X-ray powder diffractogram and is plotted versus temperature in Fig. 13. As can be seen in Fig. 13, the grain size of β-SiC heat-treated between 1200 and 2000°C is in the nm-range. Consequently, the β-SiC grain

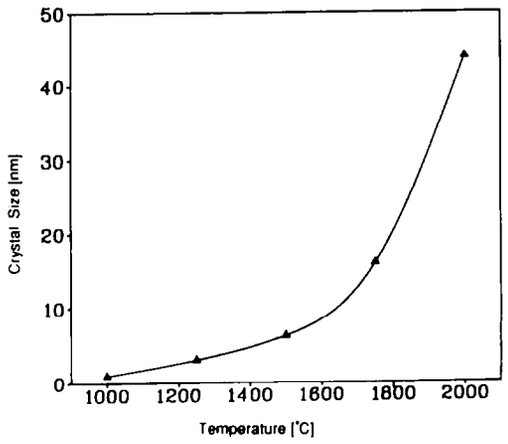

Fig. 13. Temperature dependence of the PMPS-derived β-SiC crystallite size. Isothermal hold at each temperature = 1 h in Ar.

growth is retarded which is related to the excess carbon content present in the polysilane derived SiC (Table 2). In addition, no phase transformation from the β- to the α-modification was observed even by annealing the sample at 2000°C in Ar.

4 Conclusions and outlook

The present studies have shown that dense or near dense silicon-based non-oxide bulk ceramic materials can be synthesized from organosilicon compounds under the following conditions:

(1) The synthesis of crack-free silicon carbonitride ($Si_{1.7}C_{1.0}N_{1.6}$) ceramic parts with 94% rel. density by the direct polymer to ceramic transformation process was demonstrated. An infusible polysilazane prepared by the thermal cross-linking of a commercially available organoelement polymer was used as the starting material. The annealed polymer is ball-milled and sieved, isostatically pressed to polymer green bodies and finally pyrolyzed in Ar. The method is especially suitable for the fabrication of bulk ceramics other than fibers. The main advantages of this novel process compared to the conventional method for the production of Si_3N_4- and SiC-based ceramics are:
- low processing temperature of about 1000°C
- densification without sintering aids,
- low solid-phase density (2·33 g/cm^3) of the resulting ceramic, and
- synthesis of metastable solid solutions in the ternary system Si–C–N.

As-synthesized silicon carbonitride bulk ceramic was amorphous and single phase. The material produced was thermally stable in nitrogen up to 1400°C, had a hardness, HV, of 10 GPa, and a maximum bending strength value of 370 MPa determined in samples with 6% open porosity. Additive-free silicon carbonitride is expected to be a candidate material with high temperature creep resistance.

(2) Bulk ceramics based on crystalline polymorphs comprised of SiC, Si_3N_4, and Si_2N_2O were prepared by the liquid phase sintering of polymer-derived amorphous ceramic powders. Pyrolysis of polysilazanes at 1000°C in Ar gave metastable silicon carbonitride powders with homogeneous distribution of the constituents Si, C and N. During the course of the sintering of these powders attrition milled in isopropanol with Al_2O_3 and Y_2O_3 as oxide additives, the thermodynamically stable phases, β-Si_3N_4 and β-SiC, were formed *in situ* and dense Si_3N_4/SiC-composites were obtained. Similarly, dense Si_3N_4 and Si_2N_2O bodies were produced by the liquid phase sintering of amorphous Si_3N_4 powders obtained by pyrolysis of polysilazane in ammonia.

(3) Polysilane/silicon nitride powder blends have been used to reduce the high shrinkage associated with the density increase from the Si-polymer (ca. 1·1 g/cm^3) to the Si-ceramic (ca. 3·2 g/cm^3) during pyrolysis. The polysilane PMPS used in this work resulted in the *in situ* formation of $SiC_{2.0}$. During liquid phase sintering of the PMPS/Si_3N_4-powder mixture, β-SiC crystals were formed and were embedded inter- and intragranular in the Si_3N_4-matrix.

Due to the fact that Si-based polymers such as polysilanes and polysilazanes are now commercially available, the polymer pyrolysis process can be considered as an alternative method, with respect to the traditional technology, for the production of various Si-based non-oxide ceramics in large quantities. In addition, novel type of non-oxide ceramic materials such as the solid solutions of silicon carbonitrides and *in situ* crystallized Si_3N_4/SiC micro-, nano- and micro/nano-composites can be synthesized.

Acknowledgements

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