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REVIEW

Cyclosilazanes and borazines: polymer precursors to silicon- and boron-containing ceramics

Bettina Jaschke,[1] Uwe Klingebiel,[1]* Ralf Riedel,[2] Nataša Doslik[3] and Rainer Gadow[3]

[1]Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany
[2]Fachbereich Materialwissenschaft, Fachgebiet Disperse Feststoffe, Technische Universität Darmstadt, Petersenstr. 23, D-64287 Darmstadt, Germany
[3]Institut für Fertigungstechnologie keramischer Bauteile, IFKB, Universität Stuttgart, Allmandring 5b, D-70569 Stuttgart, Germany

The chemistry of cyclosilazanes and borazines is a topic of current interest in view of preceramic polymers which yield on pyrolysis various useful ceramic materials, e.g. silicon and boron carbide, silicon and boron nitride, and ternary or quaternary mixtures of these materials. These materials are hard and have high oxidative and thermal stability. Other useful properties are resistance to corrosion, thermal shock and creep, low electrical conductivity and low coefficient of thermal expansion. One of the best application prospects is the use of the preceramic polymers as protective coating material for carbon fibres. Copyright © 2000 John Wiley & Sons, Ltd.

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1 INTRODUCTION

Ceramics are not only candidate materials for engine and turbine construction, but also for cutting tools and biomedical devices. Moreover, ceramics also have interesting magnetic or optical properties which are utilized for functional applications. However, the main disadvantages of ceramics are their brittleness and insufficient reproducibility of their excellent properties. The former is due to the predominant ionic or covalent nature of the chemical bonding in ceramic compounds, while the latter is due to the complex fabrication procedure involved in the synthesis of ceramic powders, and the processing, shaping, and sintering of fine ceramic powders. Recently, these serious handicaps can be reduced by controlling the microstructure developed during sintering and by simple improvements of single manufacturing steps. Accordingly, for example, the mechanical properties of silicon nitride (Si_3N_4)-based ceramics have been clearly enhanced, and Si_3N_4 is now applied in engine components in the form of a turbocharger rotor, glow plug, swirl chamber or rocker arm[1,2] (Table 1).

One main future target in material science for the 21st century is the development of ceramic-based advanced materials enabling high-efficiency use of energy resources which exert a minimal burden on the environment and that will help energy conservation. For example, advanced materials are now being developed for use at 1350 °C to over 1500 °C, enabling combustion without NO_x formation. Therefore, significant improvements of ceramic-based material properties, especially in the high-temperature range, are required and are expected to be achieved by novel fabrication techniques and by the synthesis of new materials. In order to provide tailor-made material properties, the starting ceramic powders have to be optimized

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* Correspondence to: Uwe Klingebiel, Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany.
E-mail: uklinge@gwdg.de
† Correspondence to: Fachbereich Materialwissenschaft, FG Disperse Feststoffe, TU Darmstadt, Petersenstr. 23, D-64287 Darmstadt, Germany.
E-mail: dg9b@tu-darmstadt.de
E-mail: ifkb@po.uni-stuttgart.de
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Table 1 Advanced ceramics and their applications

Material	Typical applications
Carbides	
SiC	Engines, machinery, cutting tools, metallurgy
B_4C	Wear, high-temperature thermocouples (B_4C/C)
Nitrides	
BN	High-temperature lubricant (h-BN), cutting tools (c-BN)
Si_3N_4	Parts in heat engines: turbocharger rotors, glow plugs, swirl chambers, rocker arm pads (in service); valves and piston pins (in development)

by increasing the purity and controlling the morphology, crystallinity and composition, which in turn influence to a great extent the phase composition and microstructure of the densified materials. In particular, chemical methods such as chemical vapour deposition (CVD), sol–gel technology and polymer pyrolysis have been used for the production of high-purity ceramic materials alongside traditional powder technology. Numerous reviews have been published on these subjects in the last ten years.[3–9]

2 POLYMER PYROLYSIS

The common feature of the chemical methods mentioned is the transformation of molecules to non-metallic, inorganic solids. Basically, in the case of CVD, low-molecular-weight compounds with high volatility are decomposed in the gas phase and are used not only for the formation of oxide or non-oxide ceramics, but also for the synthesis of metals and semiconductors. In contrast, the sol–gel and the polymer pyrolysis process employ inorganic–organic polymers which are transformed to the ceramic preferentially via the liquid or solid state. The sol–gel route is suitable for the synthesis of oxide ceramics, whereas the polymer pyrolysis route is applied largely for the preparation of non-oxide ceramics.

In general, technical synthesis of advanced ceramic materials utilizes traditional inorganic solid-state reactions operating at high temperatures. Accordingly, SiC, for example, is synthesized by the reaction of silica with carbon (Acheson process) at $T > 2000\,°C$. Si_3N_4 is fabricated either by reaction of the elements or by carbothermal reduction of silica and nitridation at 1500 °C. Since the works of Verbeek and Winter in Germany and Yajima *et al.* in Japan, both published in the 1970s, and Seyferth in USA in the 1980s, it is known that non-oxide ceramics can be produced at temperatures as low as 800–1200 °C by thermal decomposition of organosilicon preceramic polymers.[10–12] In particular, the polymer pyrolysis process involves the following reaction steps:

(1) Synthesis of oligomers or polymers from low-molecular weight-compounds.
(2) Enhanced chemical or thermal cross-linking of these synthesized polymers, giving high-molecular-weight compounds suitable for polymer to ceramic transformation with high yields.
(3) Pyrolysis of the cross-linked polymer providing the desired ceramic material, with the simultaneous loss of volatile reaction species.

Basically, polymer-derived ceramics can be obtained in higher purity than materials synthesized by traditional powder technology. This is attributed to the chemical synthesis of the polymers allowing easy purification of the reacting species by distillation or crystallization. Thus, the purity of polymer-derived ceramics is limited by the purity of the applied organoelement polymers. The viscosity of the preceramic compounds can be adjusted within a wide range by variation of the reaction conditions during polymer synthesis or by substitution of the side groups attached to the polymer backbone elements. This tailoring of the viscosity enables the processing of the polymers by well-established industrial methods such as coating and spinning of fibres.

Besides the commercial fabrication of ceramic fibres, organoelement polymers are at present under research and development for the following potential applications:

(a) synthesis of multicomponent ceramic powders and bulk materials;
(b) formation of ceramic coatings that are protective towards corrosion, abrasion etc. by dip- or spin-on coating of the polymer followed by pyrolysis of the polymer film;
(c) formation of ceramic matrices in porous structures such as fibre prepregs by polymer infiltration and subsequent pyrolysis of the infiltrated part;
(d) ceramic binders;

(e) formation of porous materials such as ceramic filtration membranes.

3 PROPERTIES OF POLYMER-DERIVED CERAMICS

3.1 Crystallization behaviour

The onset of crystallization of the metastable polymer-derived ceramics providing the thermodynamically stable phases has been found to increase, at a given temperature, with increasing number of constituent elements. Thus, materials of the binary system Si–N start to crystallize at $T = 1000$ °C forming α-Si_3N_4, whereas metastable solid solutions of the ternary and quaternary systems Si–C–N, Si–O–C–N and Si–B–C–N withstand crystallization up to 1400, 1500 or 1700 °C, respectively. At higher temperatures, polycrystalline ceramic composites composed of α- or β-Si_3N_4 and β-SiC are formed in the case of Si–C–N, Si–B–C–N with the molar ratio Si B = 3:1 provides multiphase ceramics upon crystallization, containing β-Si_3N_4, β-SiC and amorphous or α-BN and amorphous carbon or graphite. The beginning of crystallization is not only a function of the number of elements present but also depends on the molar composition. Accordingly, Si–B–C–N with a higher boron content, molar ratio Si B = 1.6:1, crystallizes at $T > 1900$ °C.[1] Moreover, the amount and type of crystallized phases depend on the composition of the amorphous ceramic, which in turn can be adjusted within a wide range by altering the polymer composition. Further systematic investigations of these phenomenologically described findings are in progress.

3.2 Thermal stability

The thermal stability of nitride-based ceramics is strongly dependent on the nitrogen partial pressure. Thus, the binary compound Si_3N_4 decomposes into the elements at $T > 1500$ °C in the absence of N_2, whereas Si_3N_4 is stable up to 1850 °C at 0.1 MPa (1 bar) N_2 pressure.

Several investigations by our group and others[1,2,13–15] have shown that the thermal stability of non-oxide Si ceramics is significantly enhanced in materials of the ternary and quaternary systems Si–B–N and Si–B–C–N. Si–B–C–N gives the best results and is thermally stable up to 1900 °C in 0.1 MPa helium. Ternary solid solution Si–C–N shows a decrease in mass at $T > 1400$ °C even at 0.1 MPa N_2 pressure, owing to the solid-state reaction of silicon nitride with elemental carbon generated in the course of crystallization or phase separation according to Eqns [1] and [2].

$$\mathrm{Si_{1.8}C_{1.0}N_{1.6}} \xrightarrow{T>1400^\circ\mathrm{C}} 0.4\mathrm{Si_3N_4} + 0.6\mathrm{SiC} + 0.4\mathrm{C} \qquad [1]$$

$$\mathrm{Si_3N_4} + 3\mathrm{C} \xrightarrow{T>1400^\circ\mathrm{C}} 3\mathrm{SiC} + 2\mathrm{N_2} \qquad [2]$$

3.3 Oxidation behaviour

Study of the oxidation behaviour of dense polysilazane-derived Si–C–N components revealed that the material resists oxidation in a pure oxygen atmosphere up to 1600 °C.[14,15] This finding is attributed to SiO_2-surface passivation, which hinders the oxidation of silicon carbonitride in the interior of the material. The mass gain owing to the formation of cristobalite (SiO_2) has been found to be less than 1 wt% during annealing of the sample at 1600 °C over 60 h in oxygen.

In the course of our work, the synthesis of molecule precursors containing the desired elements in the molecular structure is of great interest, especially for the formation of multicomponent ceramics.

4 SYNTHESIS AND PYROLYSIS OF PRECURSORS IN THE Si–N, Si–C–N AND Si–B–C–N SYSTEMS

4.1 From cyclosilazanes via crystalline silicon nitride imide Si_2N_2NH to Si_3N_4

In recent years oligo- and poly-silazanes were investigated as precursors for Si_3N_4-based ceramics.[1,2,12,17–23] Thermal decomposition under atmospheric pressure of the silazanes yields Si_3N_4 ceramics and Si_3N_4/SiC composites, depending on the pyrolysis atmosphere.[24–26] The six- and eight-membered cyclosilazanes which are used as starting material can be easily synthesized by ammonolysis of chlorosilanes. The reaction is described in Eqn [3].

$$n(\mathrm{CH_3})_2\mathrm{SiCl_2} \xrightarrow[-2n\mathrm{NH_4Cl}]{+3n\mathrm{NH_3}} 1/n[(\mathrm{CH_3})_2\mathrm{Si{-\!\!-}NH}]_n \qquad [3]$$

$$n = 3, 4$$

Because of the low molecular weight of the rings direct pyrolysis under atmospheric pressure is not possible. Therefore the reactions were carried out in an autoclave under high pressure. The cyclosilazanes react completely to crystalline silicon nitride imide, Si_2N_2NH and CH_4 according to Eqns [4] and [5].[15]

$$2[(CH_3)_2Si{-}NH]_3 \xrightarrow[-12CH_4]{+3nNH_3} 3Si_2N_2NH \qquad [4]$$

$$[(CH_3)_2Si{-}NH]_4 \xrightarrow[-8CH_4]{+2NH_3} 2Si_2N_2NH \qquad [5]$$

Complete crystallization was proved by optical transmission microscopy with crossed polarizers. The reaction product was characterized by X-ray diffraction and elemental analysis. The X-ray diffraction pattern is shown in Fig. 1(a).

The particle morphology of the crystalline Si_2N_2NH was investigated by SEM. The reaction product is a microcrystalline powder with spherical particles. The average particle size is about 0.15 μm. Si_2N_2NH reacts at temperatures above 1000 °C to give α-Si_3N_4. After annealing for 5 h at 1200 °C and for 50 h at 1300 °C the X-ray diffraction pattern clearly indicates the presence of α-Si_3N_4 apart from Si_2N_2NH. Heat treatment at 1500 °C for 5 h and at 1350 °C for 50 h yields X-ray-pure α-Si_3N_4.[14,15] Thermal decomposition of Si_2N_2NH to α-Si_3N_4 with the simultaneous loss of NH_3 is described in Eqn [6].

$$3Si_2N_2NH \longrightarrow 2\alpha\text{-}Si_3N_4 + NH_3 \qquad [6]$$

The yield of α-Si_3N_4 is 94% of the theoretical value. α-Si_3N_4 is determined by X-ray diffraction (Fig. 1b) and elemental analysis. The absence of X-ray diffraction lines corresponding to β-Si_3N_4 indicates that the $\alpha/(\alpha+\beta)$-ratio is more than 98 wt%. SEM micrographs of the synthesized α-Si_3N_4 show the presence of rod-like crystallites with a particle size of less than 0.7 μm (Fig. 2).

Compared with two commercial α-Si_3N_4 powders, namely UBE-ESP ($\approx$99% α-phase) and UBE E-10 (>95% α-phase), the α-/β-silicon nitride transformation of the α-Si_3N_4 (>98% α-phase) produced was investigated. After annealing at 1800 °C and 1 MPa N_2 pressure for 10 h, both UBE E-10 and the synthesized powder were completely transformed into β-Si_3N_4. The β-Si_3N_4 phase was identified by X-ray diffraction (Fig. 1c). In contrast UBE-ESP powder consists of about 90% α-phase and 10% β-phase. One possible reason for this contrasting crystallization behaviour is a different contamination with oxygen. However, the comparison of the three investigated powders shows that the oxygen contents are closely similar.

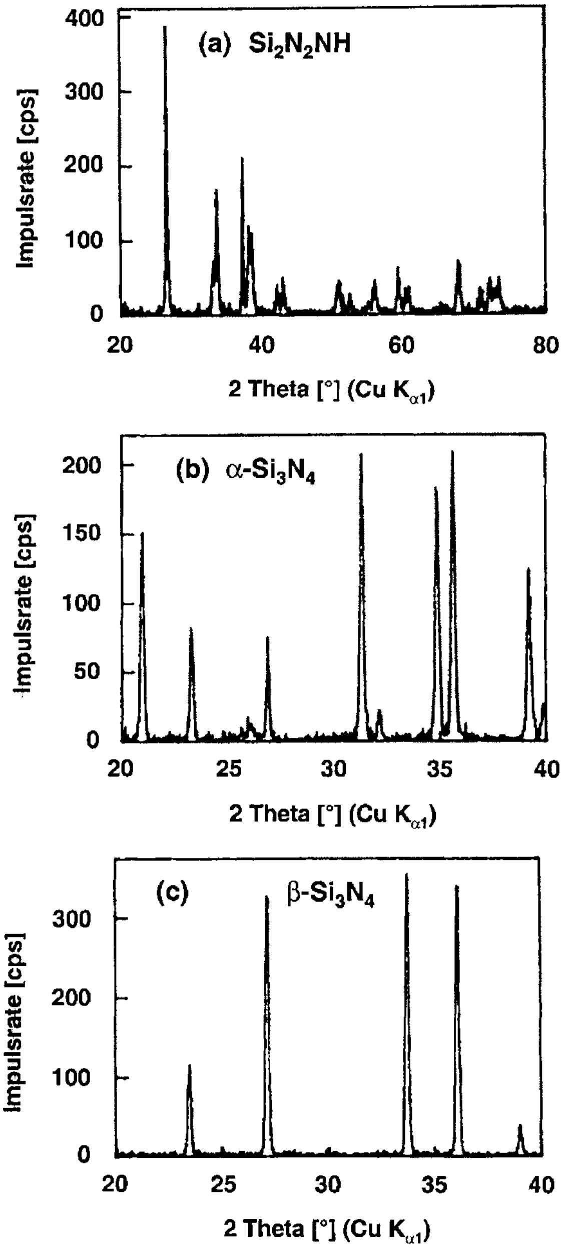


Figure 1 X-ray diffraction pattern of (a) synthesized Si_2N_2NH; (b) α-Si_3N_4 obtained at 1350 °C in 0.1 MPa N_2; and (c) β-Si_3N_4 formed after heat treatment at 1800 °C under 1 MPa N_2 pressure.[14]

Therefore we consider a homogeneous distribution of β-Si_3N_4 nuclei in the produced powder. The presence of β-Si_3N_4 nuclei accelerates the phase transformation from α-Si_3N_4 to β-Si_3N_4.

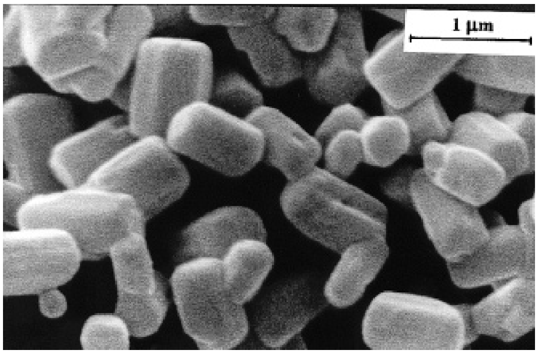


Figure 2 SEM micrograph of α-Si_3N_4 produced.[15]

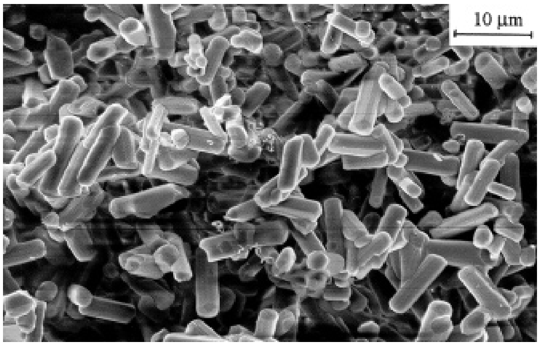


Figure 3 SEM micrograph of β-Si_3N_4 produced.

Figure 3 shows an SEM micrograph of the $(Me_2Si{-}NH)_4$-derived β-Si_3N_4. The size of the rod-like crystallites is about 9 μm.

Altogether the synthesis of binary silicon nitride by polymer pyrolysis of cyclosilazanes is relatively inexpensive. The only by-product which appears in the ammonia thermal synthesis is gaseous methane (CH_4). Methane can be easily separated from the solid reaction product Si_2N_2NH. Si_2N_2NH is considered to be an intermediate compound in the ammonolysis of $SiCl_4$, finally yielding α-Si_3N_4 at $T > 1200$ °C α-Si_3N_4 with a high ratio of α-phase (>98%) is obtained at $T = 1350$ °C. The NH_3 lost simultaneously can be used as a starting material to produce cyclosilazanes from $(CH_3)_2SiCl_2$ by ammonolysis. The α-/β-phase transformation is completely finished at 1800 °C. Therefore Si_2N_2NH derived from cyclosilazanes is a very suitable precursor for the production of α-Si_3N_4, because of the high phase purity and the low contamination of oxygen, carbon and metals.

4.2 Materials in the ternary system Si–C–N

Silicon-based non-oxide ceramics such as SiC or Si_3N_4 are candidate materials for applications in automotive or engine devices (Table 1). The most powerful route to these ceramics using the polymer pyrolysis process is the thermal decomposition of organo-substituted polysilazanes. Whereas the polysilanes have to be synthesized by the expensive dechlorination reaction of chlorodiorganosilanes, R_2SiCl_2, with sodium or potassium, the polysilazanes are much more easily accessible in high amounts by simple ammonolysis of R_2SiCl_2 and subsequent base-catalysed cross-linking of the reaction product, oligosilazane,[12] (Eqns [7] and [8]).

$$n\mathrm{CH_3SiHCl_2} + 3n\mathrm{NH_3} \xrightarrow[-2n\mathrm{NH_4Cl}]{} [\mathrm{CH_3SiH{-}NH}]_n \quad [7]$$

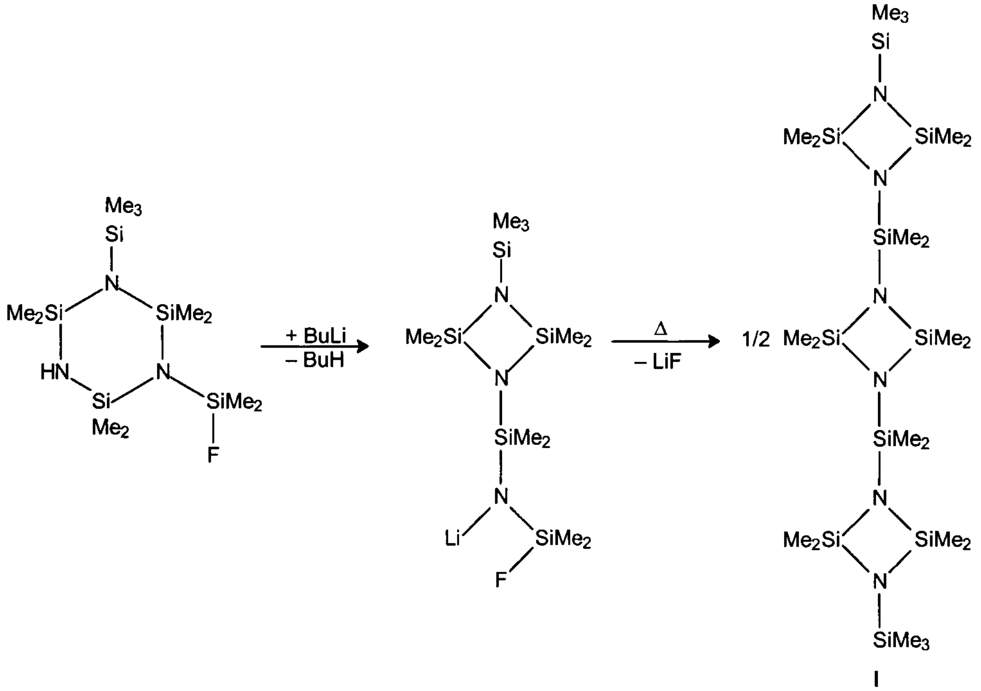
$$n[\mathrm{CH_3SiH{-}NH}]_4 \xrightarrow{\mathrm{KH}/-m\mathrm{H_2}} [\mathrm{CH_3SiH{-}NH}]_{4n-m}[\mathrm{CH_3SiN}]_m \quad [8]$$

The molecular composition of the synthesized polysilazanes can be obtained either by substitution of the methyl groups by other alkyl, aryl or vinyl groups, or by co-ammonolysis of, for example, CH_3SiHCl_2 and $(CH_3)_2SiCl_2$. Co-ammonolysis is already used for the synthesis of commercially available polysilazanes for example, Chisso Corp., Tokyo, Japan produces polysilazanes NCP 100 and NCP 200, and Hoechst AG, Frankfurt, Germany manufactures VT 50 and ET 70. Low-carbon-containing and carbon-free polysilazanes are obtained by the reaction of $[(CH_3)_3Si]_2NH$ with $HSiCl_3$ and by ammonolysis of $SiH_2Cl_2\cdot$2pyridine, respectively, and are also produced commercially.[27,28] Pyrolysis of cross-linked polysilazanes like **1** yields the desired ceramic. The applied reaction atmosphere, (argon, nitrogen or ammonia) determines the composition of the final product according to the following simplified reaction equations (Eqns [9] and [10]).

$$[\mathrm{CH_3SiH{-}NH}]_{4n-m}[\mathrm{CH_3SiN}]_m \xrightarrow{1000^\circ\mathrm{C/Ar}} \mathrm{Si}_x\mathrm{C}_y\mathrm{N}_z + \mathrm{H_2} + \mathrm{CH_4} + \ldots \quad [9]$$

$$[\mathrm{CH_3SiH{-}NH}]_{4n-m}[\mathrm{CH_3SiN}]_m \xrightarrow{1000^\circ\mathrm{C/NH_3}} \mathrm{Si_3N_4} + \mathrm{H_2} + \mathrm{CH_4} + \ldots \quad [10]$$

In contrast to CH_3SiHCl_2, dichlorodimethyl-


[11]

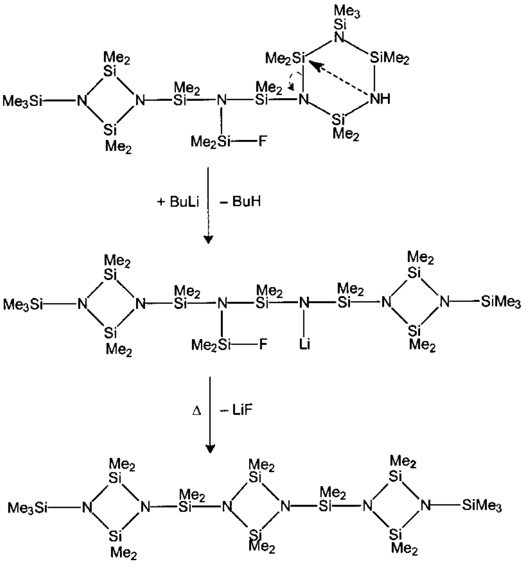
I

silane reacts with ammonia to form specific molecules, shown in Eqn [3]. The obtained cyclotri- and cyclotetra-silazanes can be substituted with further silyl groups and very easily isomerize to structural four-, six- and eight-membered rings;[29] for example, silyl-coupled four-membered rings are isolated through different reaction pathways, as follows.

(1) 1-(Fluorodimethylsilyl)2,2,4,4,6,6-hexamethyl-3-(trimethylsilyl)cyclotrisilazanes react with butyl-lithium to give the corres-ponding lithium salts. Ring contraction of the lithium salts with formation of lithiated (fluorodimethylsilyl)amino-substituted four-membered rings is observed in THF solution. The dimerization of these cyclodisilazanes with elimination of LiF is demonstrated by crystal structure determination of **I**[23,29] (Eqn [11]).

(2) The reaction of a bis(silyl)amino-coupled four- and six-membered cyclosilazane with BuLi leads to the formation of a lithium derivative with the contracted six-membered ring. LiF elimination forces a ring closure of a third cyclodisilazane (**II**) (Eqn [12] and Fig. 4).

Crystal structure determinations of the chemically identical compounds **I** and **II** show different results. For example, both are triclinic, $P\bar{1}$, but the crystallographic data were:


[12]

II

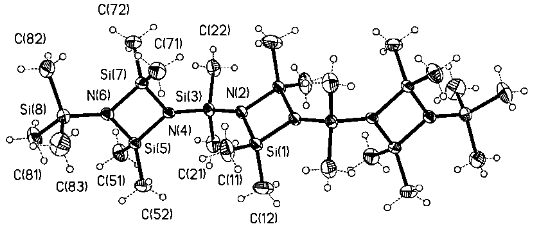


Figure 4 Structure of **II** in the crystal.

I: $a = 851.4$ pm $b = 855.8$ pm, $c = 1795.3$ pm;
$\alpha = 87.96°$, $\beta = 78.78°$, $\gamma = 61.52°$; $Z = 1$.
II: $a = 861.2$ pm, $b = 1463.2$ pm, $c = 1783.4$ pm;
$\alpha = 98.33°$, $\beta = 99.06°$, $\gamma = 90.58°$; $Z = 2$.

The silyl-coupled rings are stable up to 650 °C and react with NH_3 at 1100 °C to give Si_3N_4.[23] The advantages of this method are that the preparation of Si_3N_4 is at relatively low temperatures, the Si_3N_4 obtained is free of chlorine, and variation of the pyrolysis atmosphere (Ar/NH_3) allows the synthesis of Si_3N_4/SiC powders with definite C contents (Fig. 5).

The silicon carbonitrides, $Si_xC_yN_z$, can be considered as metastable solid solutions. A novel class of polymeric precursors suitable for the formation of Si–C–N ceramics are the polysilylcarbodi-imides, $[{-}R_2Si{-}N{=}C{=}N{-}]_n$, synthesized by the reaction of organochlorosilanes, R_xSiCl_{4-x} ($x = 0,1,2$), with cyanamide, $H_2N{-}CN$, as reported recently[2,30] (Eqn [13]).

The molecular structure of the silylcarbodi-imides was elucidated by single-crystal X-ray structure investigation of the tetrameric compound ($n = 4$).[30] The polysilylcarbodi-imides can be transformed in one step to amorphous and single-phase Si–C–N ceramics in a high yield without prior cross-linking. In contrast to the polysilazanes composed of alternating Si–N units, the polysilylcarbodi-imides contain alternating $Si{-}N{=}C{=}N$ units. This structural difference in the molecular precursors can result in different properties of the derived inorganic solid. The pyrolysis of $[{-}R(CH_3)Si{-}N{=}C{=}N{-}]_n$ with R = H or $HC{=}CH_2$ yields silicon carbonitride materials with different carbon contents and in about 65% ceramic yield, according to thermal gravimetric analysis of the pyrolysis reaction and according to elemental analysis of the reaction products obtained.

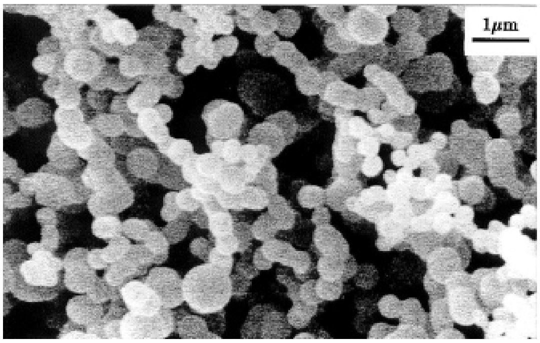
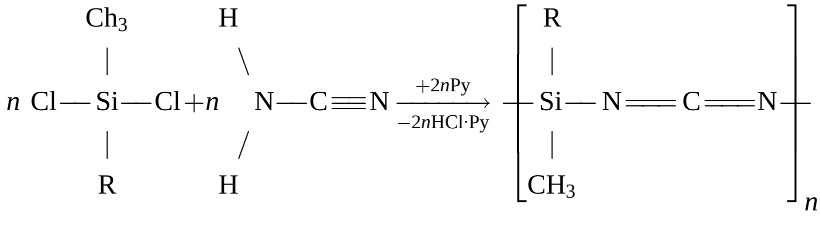


Figure 5 SEM micrograph of Si_3N_4 obtained from **I** in NH_3 at 1100 °C.

Furthermore, the reactive carbodi-imide group present in the novel type of silicon polymer can be utilized for further chemical reactions such as hydrosilylation or hydroboration. The former reaction can yield higher cross-linking of the polymer and can be applied for adjusting the viscosity to one relevant for technical application. The latter reaction results in the formation of boron-containing silicon polymers which can be thermally decomposed to silicon boron carbonitrides, materials in the quaternary system Si–B–C–N.

4.3 Materials in the quaternary system Si–B–C–N

Composite ceramics composed of two or more binary carbides or nitrides are of great interest with respect to design materials with tailor-made proper-



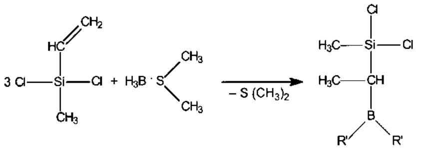
$$n\,\mathrm{Cl{-}\underset{R}{\overset{Ch_3}{Si}}{-}Cl} + n\,\mathrm{\underset{H}{\overset{H}{N}}{-}C{\equiv}N} \xrightarrow[-2n\mathrm{HCl\cdot Py}]{+2n\mathrm{Py}} \left[-\mathrm{\underset{CH_3}{\overset{R}{Si}}{-}N{=}C{=}N}-\right]_n \qquad [13]$$

$R = H, CH_3, CH = CH_2$; Py = pyridine

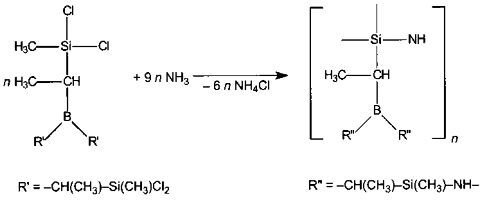
ties. However, densification by sintering of mixtures of binary ceramic powders is insufficient and leads to inhomogeneities in the final products. Therefore, the idea is to use metastable and single-phase multicomponent powders as starting materials. In this case, distinct binary phases have to be developed *in situ* during sintering by phase separation or crystallization.

However, multielement ceramic materials are difficult to synthesize by traditional methods owing to the thermodynamic instability of their solid solutions, especially of those in the ternary and quaternary systems Si–(E)–C–N with E = Al, B, P, Ti or Zr considered in the course of our work. In contrast, again the polymer pyrolysis route enables the synthesis of this type of metastable solid solution, provided that suitable molecular precursors are available.

The synthesis of heteroelement molecules that can be subsequently reacted to polymers can be accomplished, for example by hydroboration of dichloromethylvinylsilane. The reaction product formed according to Eqn [14] is a molecular compound[31] containing both boron and silicon in the molar ratio of 1:3 which can then be polymerized by ammonolysis to polyborosilazanes (Eqn [15]).



[14]

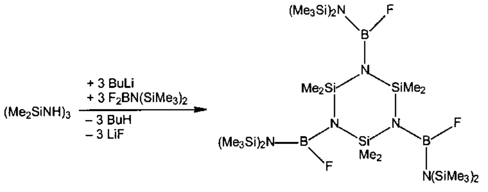


[15]

Pyrolysis of the novel polymer at 1000 °C in argon provides an amorphous ceramic material in the quaternary system Si–B–C–N in a high yield. The analysis of the composition of the polymer-derived ceramic shows that the molar ratio B Si remains unchanged after thermal decomposition.

In course of our work with cyclosilazanes, we also investigated molecular boron-containing silazanes as precursors for the formation of materials in the quaternary system Si–B–C–N.[14,15,23]

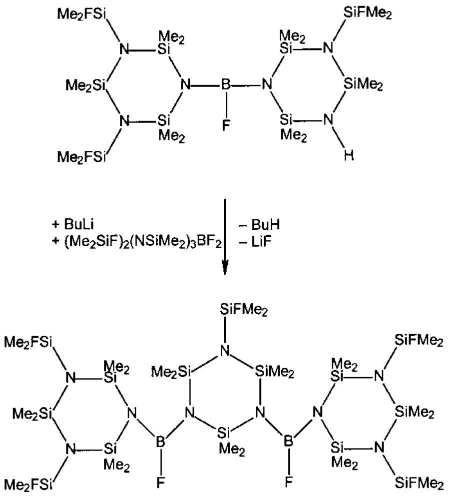
Hexamethylcyclotrisilazanes and their lithium derivatives react with $F_2BN(SiMe_3)_2$ to give the corresponding mono-, bis- and tris-fluoroborylbis(trimethylsilyl)amino]hexamethylcyclotrisilazanes (**III**).[14,15,32] The six-membered N_3Si_3 ring adopts a distorted boat conformation with normal Si–N distances and planar-coordinated boron atoms[14,15] (Eqn [16]).



III

[16]

Ring coupling of two six-membered rings occurs in the reaction of lithiated 1-fluorodimethylsilylhexamethylcyclotrisilazane with 1-difluoroborylcyclotrisilazane.[14,15] Three six-membered rings are coupled in the reaction of the lithium derivative of this compound and the 1-difluoroborylcyclotrisilazane (Eqn [17]). The X-ray structure determination of **IV** shows that the three six-membered SiN rings are crystallographically independent.[14,15] Unlike the NH-substituted compounds, which possess a planar annular structure, none of the Si_3N_3 rings shows planarity. The average deviation of the six ring atoms from the least-squares planes are 28.9 pm, 28.1 pm, and 26.5 pm, respectively. The conformation of the cyclotrisilazanes allows a description as a distorted boat form. Endocyclic SiN bond lengths (173.0–176.6 pm) are slightly



[17]

IV

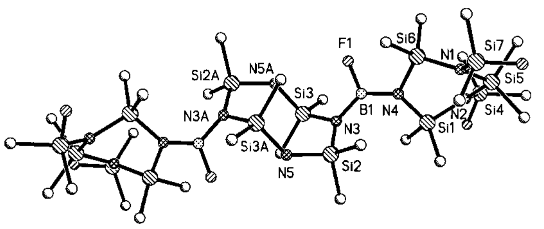
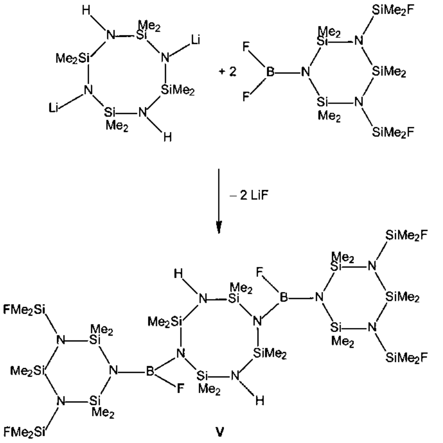


Figure 6 Molecular structure of **V** in the crystal.[33]

larger than exocyclic bond lengths (171.0–173.1 pm). The geometry of the boron and nitrogen atoms is almost planar and the sum of angles at the boron atoms is 360.0 °; the average sum of angles at the nitrogen atoms is 358.2 °.

Dilithiated octamethylcyclotetrasilazane reacts with difluoroboryl-substituted cyclotrisilazanes in an analogous reaction to Eqn [17] to give BF-coupled 6–8–6-membered cyclosilazanes **V** (Eqn. [18]).[33]



[18]

The conformation of the atoms of the eight-membered ring can be described as a chair with the atoms N(3), Si(2), N(5), N(3a), Si(2a), and N(5a) nearly in a plane. Si(3) and Si(3a) are 94 pm above and below this plane respectively. The six-membered N_3Si_3 rings adopt a distorted boat conformation (Fig. 6).[33]

4.4 Pyrolysis of III, IV, and V

Owing to their molecular composition, compounds **III–V** are suitable precursors for the synthesis of Si_3N_4/SiC/BN composites. The reactions in Eqns [19], [20] and [21] represent the idealized overall thermal decomposition reaction (pyrolysis) from the oligomer to the ceramic material.

$$\mathit{III}: C_{24}H_{72}B_3F_3N_6Si_9 \rightarrow 3\,BN + \frac{3}{4}Si_3N_4 + \frac{63}{4}SiC + xC + \text{volatiles} \qquad [19]$$

$$\mathit{IV}: C_{28}H_{84}B_2F_7N_9Si_{14} \rightarrow 2\,BN + \frac{13}{4}Si_3N_4 + \frac{83}{4}SiC + xC + \text{volatiles} \qquad [20]$$

$$\mathit{V}: C_{28}H_{86}B_2F_6N_{10}Si_{14} \rightarrow 2\,BN + 2\,Si_3N_4 + 8\,SiC + xC + \text{volatiles} \qquad [21]$$

At 1100 °C, **III–V** were pyrolysed under an argon atmosphere to give a black and X-ray-amorphous ceramic residue, with fluorosilanes and alkanes as volatiles. The product formed is composed of powder particles and a coating on the reaction tube wall, indicating that **III–V** are thermally decomposed via both solid-state pyrolysis and gas-phase decomposition. The yield of the powder derived from the solid-state pyrolysis of the molecular compounds **III, IV** and **V** and that of the coating derived from the gas phase decomposition of the evaporated volume fractions of the precursors **III–V** are given in Table 2. It is clear therefore that for powder production compounds **III–V** have to be cross-linked before pyrolysis.

After annealing of the synthesized amorphous Si–B–C–N powders at different temperatures (1300, 1500/1600, 1700, 1800 and 2200 °C) under a nitrogen atmosphere, the crystallization behaviour was investigated by X-ray powder diffraction. In the case of **III**, crystallization occurs at 1500 °C. The reflection lines indicate the formation of cubic β-SiC. At 2200 °C, crystalline hexagonal BN is indicated from the diffraction pattern (Fig. 7).

In the case of **IV** and **V**, the synthesized Si–B–C–N powder remains amorphous up to 1600 °C. The onset of the crystallization of β-SiC is shifted to

Table 2 Yields (%) of powder derived from solid-state pyrolysis (see text)

	Yield		
Compound	Theoretical	With coating	Without coating
III	57.2	48.4	18.3
IV	59.8	52.4	25.8
V	59.6	55.8	24.5

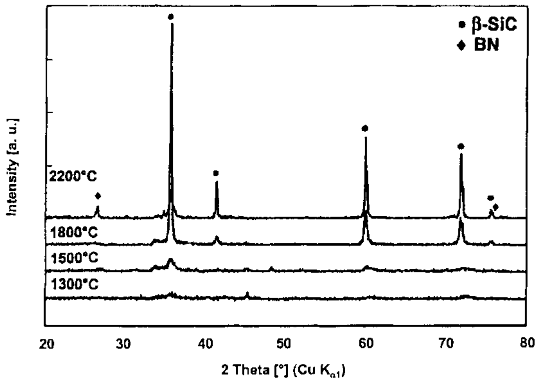


Figure 7 X-ray diffraction pattern of **III** pyrolysed at 1100 °C and subsequently annealed at 1300, 1500, 1800 and 2200 °C.[14]

higher temperatures (1700 °C) whereas the formation of crystalline h-BN is also confirmed at 2200 °C. In both cases, however, the crystallization of Si_3N_4 is completely suppressed. This finding is due to the presence of boron and to the thermodynamic instability of Si_3N_4 towards excess carbon. At 0.1 MP nitrogen pressure and at temperatures above 1440 °C, Si_3N_4 reacts with free carbon to give SiC and elemental nitrogen. Taking into account the reactions in Eqn [19]–[21], it is expected that formation of a considerable amount of excess carbon, by the crystallization of the amorphous Si–B–C–N material, hinders the formation of Si_3N_4.

In contrast, amorphous polysilazane-derived ceramics of the ternary system Si–C–N have been shown to crystallize at $T \geq 1440$ °C under 0.1 MPa nitrogen pressure.[34] The enhanced thermal stability of materials in the quaternary system Si–B–C–N with respect to the onset of crystallization, as found in this work, is of great technological interest since the high-temperature application of amorphous, polymer-derived ceramics such as, for example, inorganic fibres may be limited by the onset of crystallization. The difference between the onset of crystallization of the silicon boron carbonitride derived from **III, IV** and **V** may be caused by the different molecular structures of the precursors.

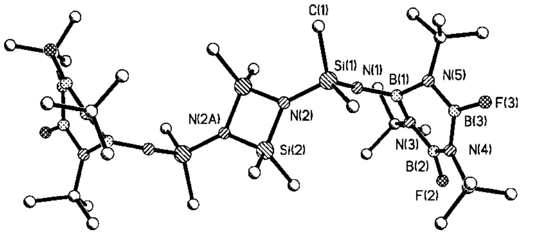


Figure 8 Structure of **VI** in the crystal; selected bond lengths (pm): B(1)–N(1) 141.6, B(1)–N(3) 147.4, B(2)–N(3) 142.1, Si(1)–N(2) 171.8, Si(2)–N(2) 174.2, Si(1)–N(1) 175.0 (R. Jaschke and U. Klingbiel, unpublished results).

4.4.1 Experimental details

The pyrolyses were carried out under a protective atmosphere (argon) using the Schlenk technique. Compounds **III–V** were pyrolysed in quartz glass tubes at 1100 °C for 5 h.

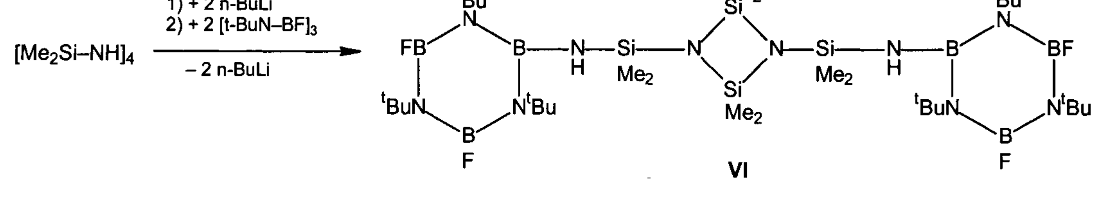
The amorphous ceramic powders obtained were heat-treated for 5 h in a 0.1 MPa nitrogen atmosphere at different temperatures (1300, 1500/1600, 1700, 1800 and 2200 °C) in a graphite furnace. Phase analysis was conducted by X-ray diffraction with Cu-K radiation ($\lambda = 154.056$ pm) using a scintillation counting detector.

5 SYNTHESIS OF PRECURSORS IN THE Si–B–N AND Si–N–C–B SYSTEMs

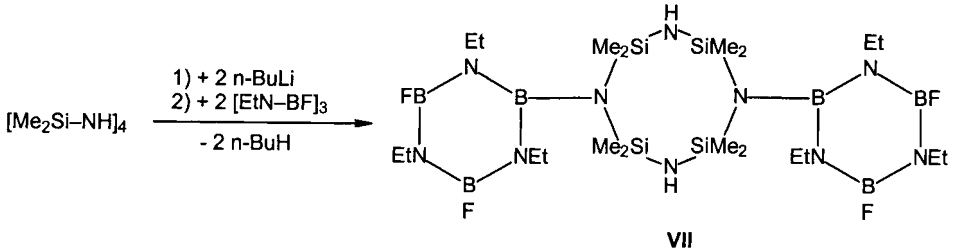
In the coupling of cyclosilazanes and borazines in different ratios, we are able to prepare precursor molecules for the polymer pyrolysis in nearly every molar ratio of the silicon, boron and nitrogen atoms. By interconversion reactions the cyclosilazanes form four-, six- or eight-membered rings.

5.1 Reactions of [Me$_2$Si—NH]$_4$ with fluoroborazines

Compound **VI** (Si B N = 2:3:5) is formed in the reaction of dilithiated eight-membered octamethyl-



[22]



VII

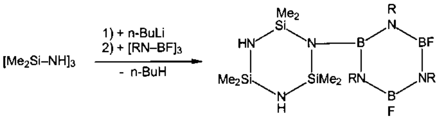
[23]

cyclotetrasilazane with 1,3,5-tri-*t*-butyl-2,4,6-trifluoroborazine (Eqn [22]).

Compound **VI** (Fig. 8) contains non-planar N-atoms ($\sum$N = 358.2 °–359.3 °) in the B–N ring system. The central cyclodisilazane is formed in an anionic rearrangement of the eight-membered ring system. The ring contraction depends on the bulkiness of the substituents of the borazine ring; it does not occur when borazines with smaller substituents (such as ethyl) are used (Eqn [23]) (B. Jaschke and U. Klingebiel, unpublished results).

5.2 Reactions of $[Me_2Si—NH]_3$ with fluoroborazines

Six-membered Si–N and B–N rings (**VIII** and **IX**) are coupled according to Eqn [24] (Si B N = 1:1:2).

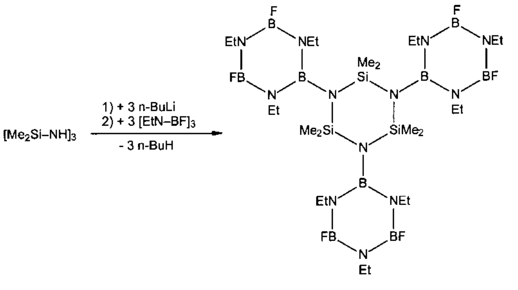


[24]

VIII, IX

R = Me, Et

An anionic rearrangement can be observed in the coupling of two bulky fluoroborazines with hexamethylcyclotrisilazane to form **X** (Si B N = 1:2:3) (Eqn [25]). Interestingly, compound **X** (Fig. 9) again contains non-planar N-atoms; for example, the sum of angles of N(1) is 352.2 °. The angles around the atoms N(4), N(8) and N(9) vary between 358.2 ° and 359.2 ° and those of B(1) and B(4) between 359.0 ° and 359.4 °. Trilithiated hexamethylcyclotrisilazane reacts with 3 equiv. of 1,3,5-triethyl-2,4,6-trifluoroborazine to give compound **XI** (Si B N = 1:3:4) (Eqn [26], Fig. 10) (B. Jaschke and U. Klingebiel, unpublished results).



[26]

XI

Compounds with a higher ratio of silicon are obtained in reactions [27] and [28]. Compounds

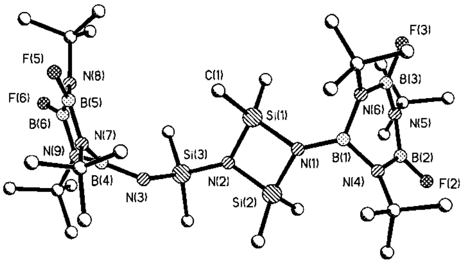
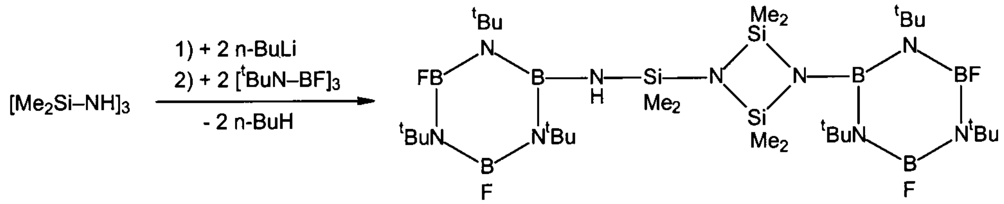


Figure 9 Structure of **X** in the crystal; selected bond lengths (pm): N(1)–B(1) 141.7, N(3)–B(4) 140.5, N(6)–B(1) 148.4, N(6)–B(3) 140.8, Si(1)–N(1) 177.0, Si(3)–N(2) 171.9, Si(3)–N(3) 174.8 (B. Jaschke and U. Klingebiel, unpublished results).



X

[25]

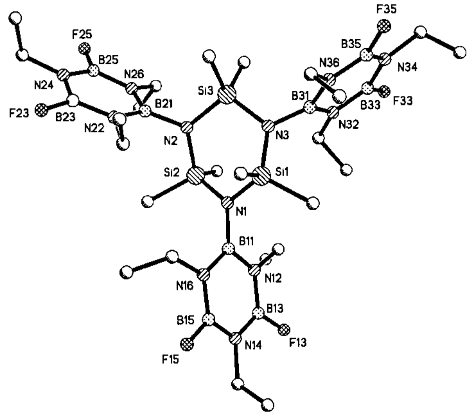
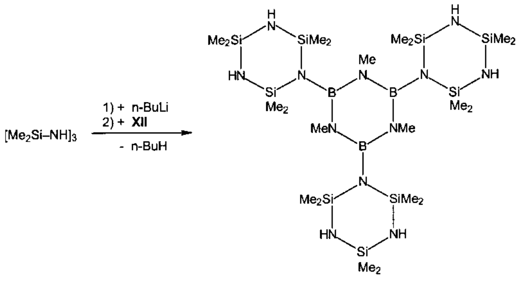


Figure 10 Structure of **XI** in the crystal; selected bond lengths (pm): Si(1)–N(1) 174.9(2), N(1)–B(11) 149.3(3), B(11)–N(12) 144.4(3), B(13)–N(14) 141.3(4); selected angles: N(3)-Si(1)-N(1) 108.88(10) °, Si(2)-N(1)-Si(1) 119.44(11) °(B. Jaschke and U. Klingebiel, unpublished results).

XII and **XIII** (Si B N = 2:1:3) can be prepared according to Eqn [27] (B. Jaschke and U. Klingebiel, unpublished results). In **XIII** (Fig. 11) the exocyclic B–N bonds (N(4)–B(2) and N(7)–B(3)) are longer than the endocyclic ones. Compounds which are totally symmetric and free of halo atoms can be formed in reactions of cyclosilazanes and borazines in a 3:1 ratio: **XIV** (Si B N = 3:1:4) (Fig. 12). Is obtained according to Eqn [28] (B. Jaschke and U. Klingebiel, unpublished results).



XIV

[28]

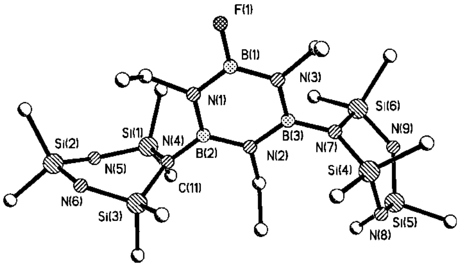


Figure 11 Structure of **XIII** in the crystal; selected bond lengths (pm): N(1)–B(1) 141.8, N(1)–B(2) 144.6, N(4)–B(2) 147.3, N(4)–Si(1) 173.4, N(5)–Si(2) 172.1 (B. Jaschke and U. Klingebiel, unpublished results).

Again the exocyclic B–N bonds are found to be longer (2.4 pm) than the endocyclic ones.

5.3 Reactions of hexamethyldisilazane with fluoroborazines

Another way to prepare precursor molecules with-

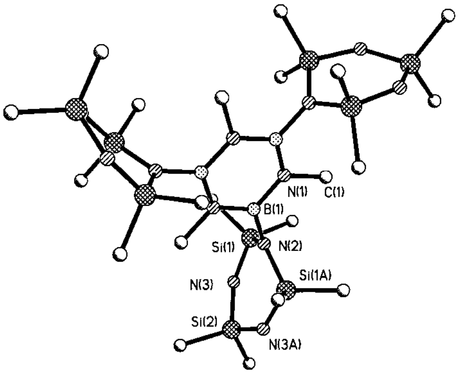
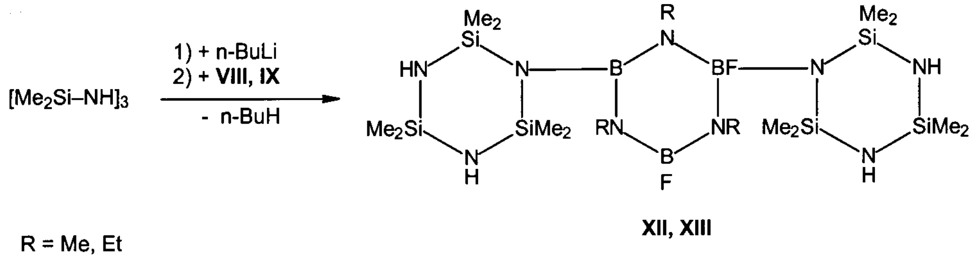
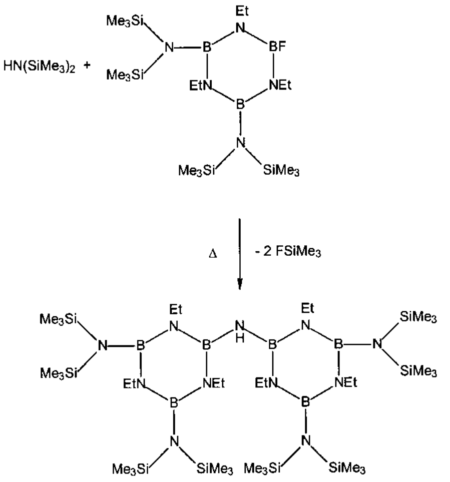


Figure 12 Structure of **XIV** in the crystal; selected bond lengths (pm): N(1)–B(1) 144.5, N(2)–B(1) 146.9, N(2)–Si(1) 172.4, N(3)–Si(1) 167.5, N(3)–Si(2) 167.4 (B. Jaschke and U. Klingebiel, unpublished results).



[27]

out halo atoms for Si–B–C or Si–B–C–N ceramic materials is by the reaction of fluoroborazines with hexamethyldisilazane. Compound **XV** (Si B N = 4:3:5.5) is prepared in this way (Eqn [29], Fig. 13) (B. Jaschke and U. Klingebiel, unpublished results).



[29]

XV

6 APPLICATIONS

Polymer ceramic precursors can be applied as bulk materials matrix components in refractory composites and last but not least as protective coatings for wear-or oxidation-sensitive substrates. Carbon fibres are found today in a wide range of applications as reinforcing components in ceramic and metal matrix composites, with characteristic features such as high tenacity and elastic modulus. In spite of the excellent mechanical properties at high temperatures a drawback is their sensitivity against oxidation and chemically active environments. Therefore commercially available fibres are not appropriate for application at high temperatures. Various coating technologies have been developed to build protective and adhesion-controlling surface layers.[35,36]

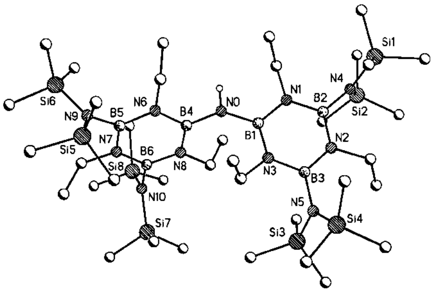


Figure 13 Structure of **XV** in the crystal; selected bond lengths (pm): N(0)–B(1) 143.8, N(1)–B(1) 143.9, N(1)–B(2) 143.7, N(4)–B(2) 146.9, N(4)–Si(2) 173.8 (B. Jaschke and U. Klingebiel, unpublished results).

Promising prospects for new protective coating materials that are stable at high temperatures are shown by Si–B–C–N compounds.

Crack-free silicon-based ceramic coatings on carbon fibres are obtained by dip-coating and subsequent curing and thermal treatment. This kind of process was used for primary investigations and optimization of the coating process and of the precursor properties.[37,38] The coating experiments are in process of being transfered to a continuously running pilot plant for liquid-phase carbon fibre coating. The results presented give an insight into

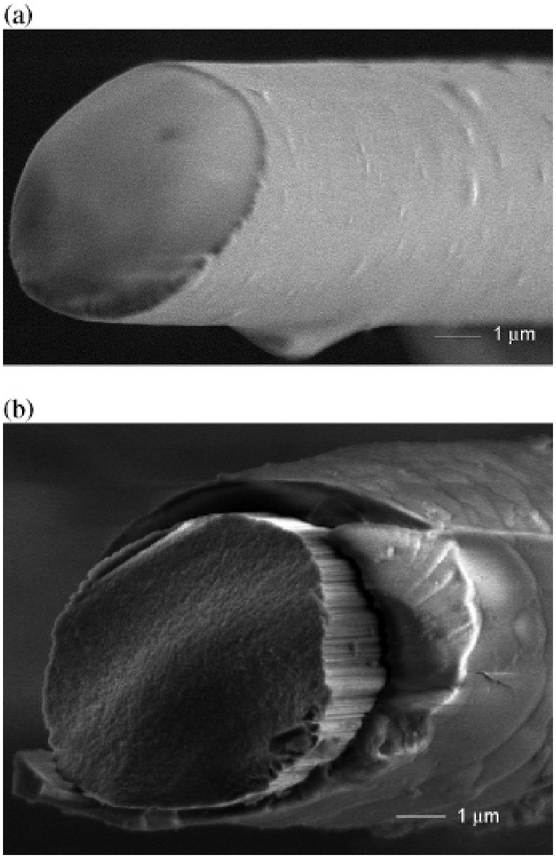


Figure 14 SEM micrographs of carbon fibre monofilaments dip-coated in $[(CH_3)_2Si—NH]_4$ under an argon atmosphere after pyrolysis (a) at 500 °C; (b) at 700 °C.

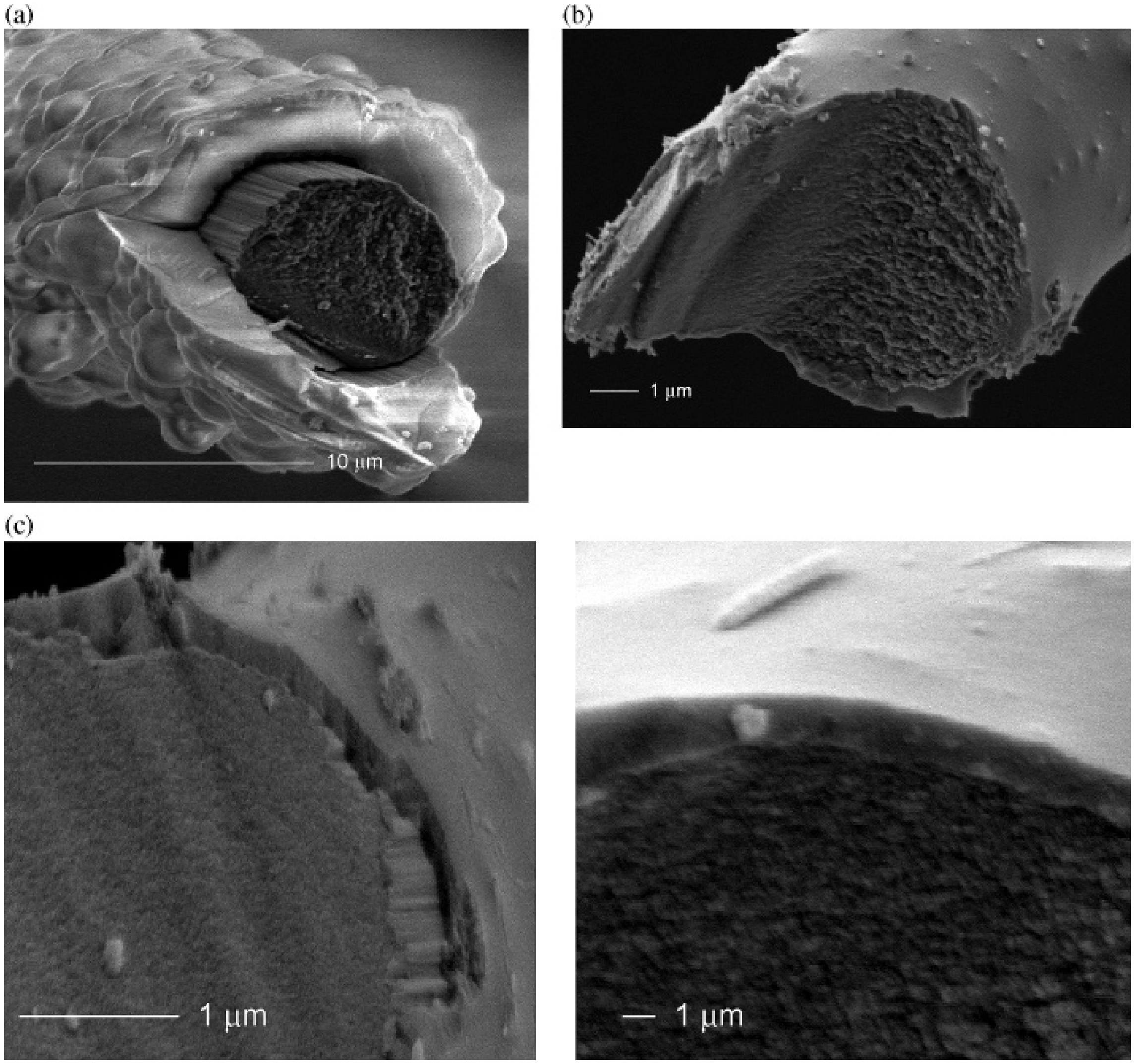


Figure 15 SEM micrographs of carbon fibre monofilaments dip-coated in $[(CH_3)_2Si—NH]_4$ under an NH_3 atmosphere after pyrolysis (a) at 800 °C; (b) at 900 °C (detail).

the application possibilities of recently developed precursors as coating components on carbon fibres.

Series of coating tests have been made with the preceramic material $[(CH_3)_2Si—NH]_4$ in argon and NH_3 atmospheres with temperature as the varied parameter. In an argon atmosphere the ideal temperature range to obtain crack-free homogeneous monofilament coating is relatively low, between 500 and 700 °C (Fig. 14). The SEM micrograph of $[(CH_3)_2Si—NH]_4$ after pyrolysis at 700 °C still shows a crack-free coating on the carbon fibre, but with a much denser structure. At higher temperatures the coating begins to shrink and microcrack formation occurs. Under an NH_3 atmosphere a completely opposive tendency has been observed in experiments with $[(CH_3)_2Si—NH]_4$. At rising pyrolysis temperatures, the coating quality is found to increase. Above 800 °C the coating becomes more homogeneous and crack-free (Fig. 15). Such coating film, 200 nm thick, shows a very strong adhesion to the carbon fibre (Fig. 15c). Experiments at higher process temperatures are still in progress, but there is strong evidence that coating homogeneity and adhesion will further improve at temperature settings of 1000 °C/1100 °C.

These studies indicate that, with optimized atmosphere and temperature parameters, $[(CH_3)_2Si—NH]_4$ is a promising preceramic material to form a ceramic protective coatings on carbon fibres.

7 CONCLUSIONS AND OUTLOOK

The transformation of organoelement molecules into polymers and then inorganic solids by polymer pyrolysis gives novel ceramic materials which cannot be synthesized by classical methods. In particular, solid solutions metastable up to extraordinarily high temperatures and multielement ceramics are the reaction products. The novel materials can be processed to fibrous or bulk materials by thermolytic decomposition of polymeric preforms at moderate temperatures, avoiding energy costs associated with the densification of crystalline ceramic powders at high temperature. The covalently bound non-oxide and silicon-based ceramics can be obtained in dense form without using additives which affect the mechanical properties at high temperatures. Amorphous, multicomponent ceramics can be crystallized *in situ*, providing micro- or nano-sized composites.

Future work is focused on the synthesis of model polymers to study the influence of the molecular structure of the precursor on the solid-state structure and microstructure of the inorganic solid formed. The preparation and characterization of novel polymers containing elements other than boron, silicon, nitrogen or carbon are of great interest with respect to the investigation of the material properties derived.

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