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REVIEW

Boron-modified Inorganic Polymers—Precursors for the Synthesis of Multicomponent Ceramics

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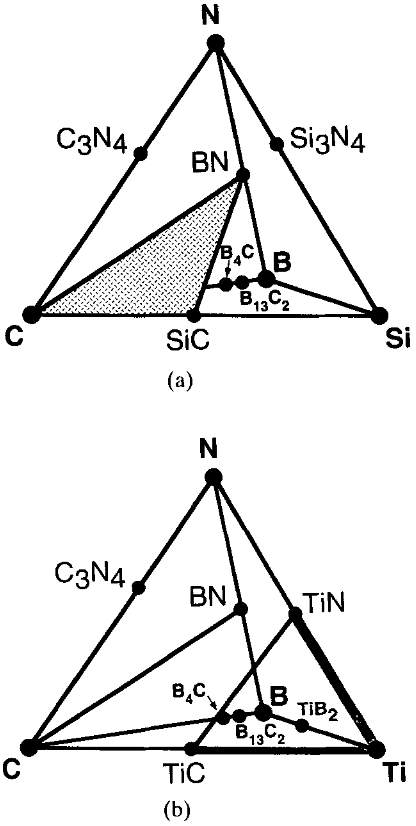
INTRODUCTION

Multiphase polycrystalline composite ceramics composed of two or more binary carbides or nitrides are of great interest with respect to designing materials with tailormade properties.[1] The densification, by sintering, of mixtures of binary ceramic powders is insufficient and leads to inhomogeneities in the final products. Therefore, one solution to this problem is to use metastable and single-phase multicomponent powders as starting materials. In this case, the distinct binary phases are developed *in situ* during densification by phase separation or crystallization.[2]

However, multielement ceramic materials are difficult to synthesize by traditional high-temperature synthesis methods such as solid-state reactions, owing to the thermodynamic instability of their solid solutions, especially of those in the ternary and quaternary systems [(E)–B–C–(N) with E = Si and Ti, and Si–B–N–O] considered in this work. In contrast, multicomponent ceramics can be synthesized in the form of metastable and single-phase solid solutions by the polymer-to-ceramic transformation route.[3,4] This method basically operates at extraordinarily low temperatures (1000–1500 °C) compared with the conventional processes used for the formation of covalently bound ceramics such as carbides and nitrides. In Fig. 1, the most relevant thermodynamically stable phases that can be formed from



(a)

(b)

Figure 1 Schematic representation of the phase diagrams of the quaternary systems (a) Si–B–C–N and (b) Ti–B–C–N. The most prominent binary compounds and some regimes of solid solutions of the materials relevant in the field of advanced ceramics are depicted. The compound C_3N_4 is presently under discussion as novel superhard material.[64,66] The shaded area in (a) represents the compositions of the materials derived from organopolyborosilazane **4** (see text) by pyrolysis at 1100 °C and subsequent annealing of the ceramic product at $T >$ 2000 °C under argon.[5]

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polymer-derived ceramics in the Si–B–C–N and Ti–B–C–N systems are illustrated by the simplified quaternary phase diagrams. Accordingly, a variety of different ceramic composites can be obtained from these single-phase and multielement amorphous solid solutions.

Moreover, solid solutions such as silicoboron carbonitride or silicoboron oxynitride are amorphous and can be considered as a novel type of glasses with significantly enhanced viscosities and, hence, rigid cross-linked three-dimensional networks compared with their oxide counterparts. In the case of multicomponent systems containing Main-Group elements exclusively, such as Si–B–C–N, crystallization starts at temperatures exceeding 1500 °C.[4–7] Simultaneously, the Si-B–C–N system exhibits an increased thermal stability with respect to pure Si_3N_4, even in nitrogen-free atmospheres.[5,8] The high onset temperature of crystallization and/or the high thermal stability are required properties, e.g. for the development of novel high-temperature-resistant ceramics with sufficient mechanical properties (fibers, coatings and bulks) to withstand service temperatures exceeding 1500 °C.[9] These materials will be desired in the future, especially for applications such as structural parts for motor engines, gas turbines, catalytic heat exchangers, cutting tools, air- and space-craft and light-weight construction.[10]

Commercial (Si_3N_4)-based ceramics are characterized by high mechanical properties such as strength, fracture toughness, creep- and oxidation-resistance at $T < 1000$ °C, and are used in engine components in the form of turbocharger rotors, glow plugs, swirl chambers or rocker arm pads.[11] The commercial realization of Si_3N_4 ceramic valves is expected in the coming years. However, the limited thermal stability and oxidation resistance of conventionally fabricated Si_3N_4 parts, due to the presence of sintering promoting oxidic secondary phases, prohibit service temperatures higher than 1300 °C. These oxide additives are located at the grain boundaries and triple junctions of the polycrystalline sintered material and impair the high-temperature properties such as creep- and oxidation-resistance.[12] Therefore, further research concerning the development of high-temperature-resistant Si_3N_4-based ceramics has to focus on the composition and reduction of the amount of secondary phase or on the synthesis of secondary-free microstructures. The latter has been realized recently by the transformation of compacted polysilazane powder into dense or nearly-dense ceramic bulk samples denoted as hybrid-processing.[8,13] The principal processing steps are illustrated by the flow chart given in Fig. 2. In contrast to the traditional powder processing for the synthesis of ceramic parts, the novel hybrid processing enables the fabrication of oxide-additive-free Si_3N_4-based ceramics and composites and is, therefore, a promising route for the synthesis of ultrahigh-temperature-resistant materials.

Finally, the directed *in-situ* crystallization of the transient amorphous phases into nano-sized ceramics and ceramic composites provides access to materials with extraordinary properties such as superplasticity, enhanced mechanical strength or improved oxidation-resistance and is presently under investigation.[1,14,15] Thus, for example, dense micro/nano bulk composites composed of α- or β-Si_3N_4 microparticles and nano-sized β-SiC grains were obtained after sintering and crystallization of amorphous polyorganosilazane-derived silicon carbonitride samples.[14,15] A typical section of such a composite microstructure is depicted in the scanning electron microscopy (SEM) micrograph in Fig. 3.

In the present work, the synthesis of boron-modified inorganic polymers and their use as precursors for the synthesis of boron containing high-temperature-resistant carbonitrides and oxynitrides are reviewed.

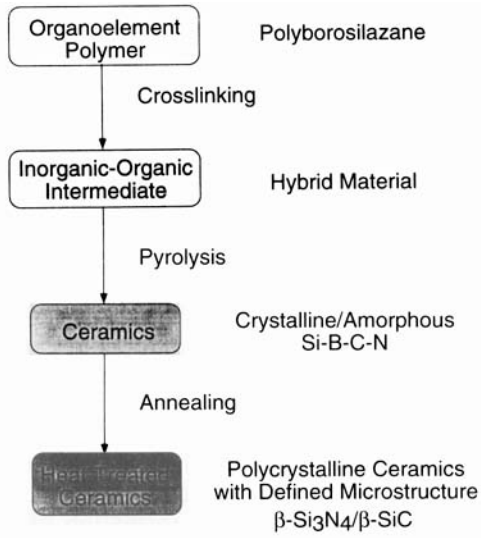


Figure 2 Flow diagram representing the hybrid processing of ceramics starting from organoelement polymers (after Ref. 13).

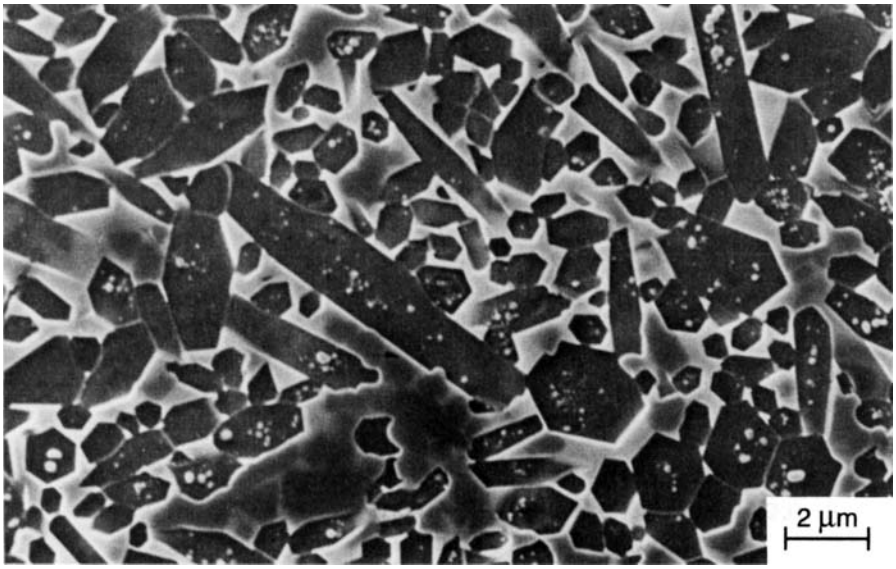


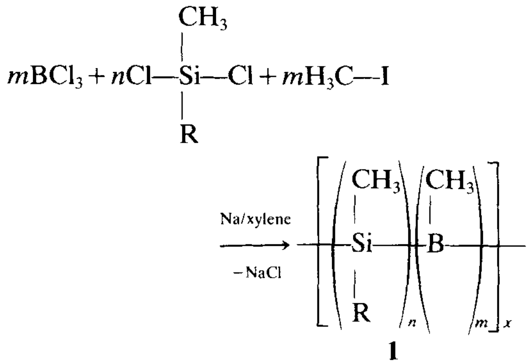
Figure 3 SEM micrograph showing a β-Si_3N_4/β-SiC micro-/nano-composite synthesized by sintering and *in-situ* crystallization of polyhydridomethylsilazane-derived silicon carbonitride bulk material at 1850 °C under nitrogen and in the presence of Al_2O_3 and Y_2O_3 as sintering additives.[14]

TERNARY AND QUATERNARY BORON-CONTAINING SILICON CARBIDE/NITRIDE CERAMICS

Materials in the ternary system Si–B–C

The first reaction pathways to ceramic precursors for the system Si–C–B were reported by Yajima *et al.*[16] These authors studied the reaction of dichlorodiphenylsilane with $B(OH)_3$ in the temperature range between 100 and 400 °C, which gave polyborodiphenylsiloxane. Thermally induced transformation of the reaction product resulted in the formation of an amorphous ceramic. Subsequent annealing at temperatures above 1000 °C resulted in crystallization to β-SiC- and B_4C-polycrystals.

The co-condensation of the chloroboranes BCl_3 and CH_3BCl_2 with dialkyldichlorosilanes $RR'SiCl_2$ and different amounts of CH_3I in the presence of sodium were investigated by Hsu *et al.*[17] This reaction resulted in the formation of boron-containing organosilicon polymers with an alternating Si–B polymer backbone (Eqn [1]).



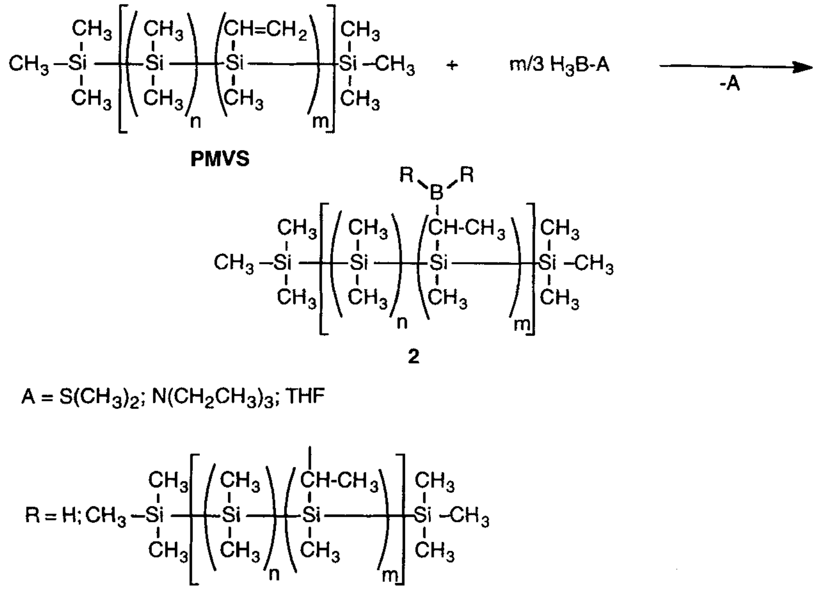
$$mBCl_3 + nCl-\underset{R}{\overset{CH_3}{Si}}-Cl + mH_3C-I \xrightarrow[-NaCl]{Na/xylene} \left[\left(-\underset{R}{\overset{CH_3}{Si}}- \right)_n \left(-\overset{CH_3}{B}- \right)_m \right]_x \quad [1]$$

1

R = methyl or vinyl

The molecular weight of the as-synthesized polymer **1** was influenced by the amount of CH_3I used in the reaction mixture. The polymer-to-ceramic conversion of **1** at 1100 °C/1 h under a nitrogen atmosphere gave black and X-ray-amorphous ceramics in the ternary Si–B–C system in 50–60 wt% yield. Depending on the amount of boron in the pre-ceramic polymers, the resulting boron content in the final ceramic material was in the 6–12 wt% range. Increasing the final pyrolysis temperature to 1300 °C provides an amorphous Si–B–C matrix with SiC polycrystals, as analysed by X-ray powder diffractometry (XRD).

A novel synthesis of polyborosilanes which avoids the use of sodium or potassium as the dechlorinating agent (see Eqn [1]) was reported by Riccitiello *et al.*[18] Accordingly, diethynyl- and divinyl-alkylsilanes were hydroborated with borane adduct compounds providing polymers with C–B bonds. Riedel *et al.* reported the hydroboration of vinyl-substituted organopolysilanes,



[2]

polymethylvinylsilane (PMVS), with various borane adduct compounds (Eqn [2]).[19]

The hydroboration reaction of PMVS leads to polysilane chains branched via B–C bridges. The molecular weight increases from $M_n = 831\ \mathrm{g\ mol^{-1}}$ in the starting polymer to $1224\ \mathrm{g\ mol^{-1}}$ in the hydroborated product **2**. Using $(CH_3)_2S \cdot BH_3$ as the hydroborating agent, the reaction starts spontaneously at room temperature whereas in the case of $(C_2H_5)_3N \cdot BH_3$ temperatures of 80–90 °C are needed. The pyrolysis at 1100 °C in argon of the boron-containing organopolysilanes obtained yields X-ray-amorphous silicoboron carbide with the empirical formula $Si_{1.7}C_{3.2}B_{0.6}$. The crystallization behaviour of the as-synthesized ceramic was investigated in the temperature range between 1000 and 2200 °C. Above 1400 °C, the ceramic starts to crystallize with the formation of ultrafine composites containing β-SiC, B_4C and graphite-like boron-containing carbon, BC_x, as analysed by transmission electron microscopy (TEM) studies.[19]

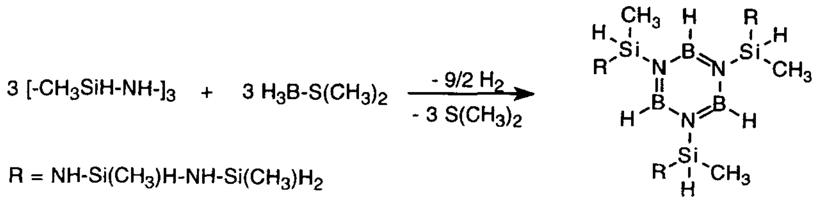
Materials in the ternary and quaternary systems Si–B–(C)–N

Composites composed of Si_3N_4 and BN exhibit excellent thermomechanical properties.[20,21] Ceramics in the ternary system Si–B–N have been prepared as thin films by CVD or hot-pressing of the distinct ceramic powders.[20] The synthesis of Si–B–(C)–N ceramics via polymer pyrolysis can be achieved by two routes.

(1) Boron- and silicon-containing monomers with functional groups can be polymerized e.g. by polycondensation.
(2) Organosilicon polymers can be reacted with boron compounds to form boron-containing organosilicon polymers.

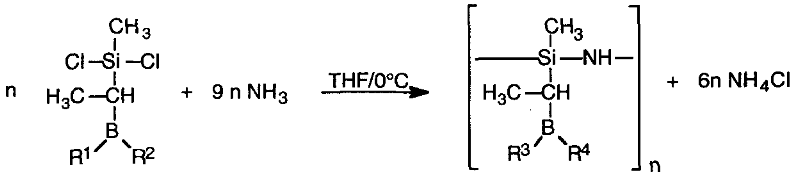
Subsequent pyrolysis under ammonia results in ceramics in the ternary system Si–B–N, whereas thermal decomposition under argon gives ceramics in the quaternary system Si–B–C–N.

Based on observations of Nöth,[22] who investigated the reaction of B_2H_6 with hexamethyldisilazane, Seyferth and Plenio[23] studied the reactions of oligomeric silazanes, $[CH_3SiH\text{—}NH]_n$, with borane adducts. On mixing the starting materials in toluene as the solvent, the reaction begins with the elimination of H_2. The authors found that increasing the amount of borane results in the formation of higher cross-linked products. The presence of borazine rings in the derived polymer could be demonstrated by ^{11}B NMR spectra, which showed a characteristic broad resonance signal between 32 and 34 ppm. Accordingly, the reaction path shown in Eqn [3] was suggested. Thermal decomposition at 1000 °C under flowing ammonia of the monomethyl-substituted polyborosilazanes obtained gave up to 90 wt% ceramic yield with a molar composition of $1\,BN + 0.54\,Si_3N_4$. If cyclo-$[(CH_3)_2Si\text{—}NH]_n$ ($n = 3, 4$) is reacted with $H_3B \cdot S(CH_3)_2$ the reaction rate and the driving force for borazine formation are dec-



R = NH-Si(CH$_3$)H-NH-Si(CH$_3$)H$_2$

[3]



3 **4**

R^1 = R^2 = -CH(CH$_3$)-Si(CH$_3$)Cl$_2$ R^3 = R^4 = -CH(CH$_3$)-Si(CH$_3$)-NH-

[4]

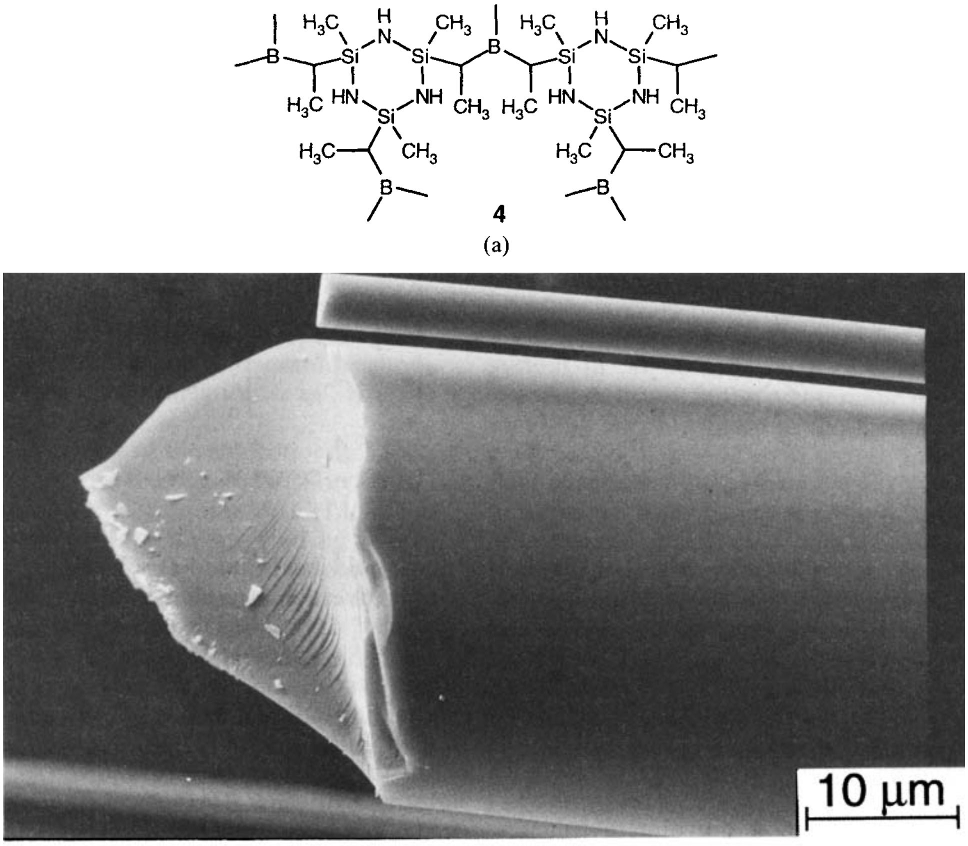
reased. As a consequence, the dimethyl-substituted polyborosilazane gave only 2 wt% ceramic yield after decomposition at 1000 °C under a stream of argon. The higher ceramic yield of the Si—H-substituted polymers results from *in-situ* cross-linking via elimination of H_2 during the heat treatment.[23]

The first organosilicoboron polymers were reported by Takamizawa *et al.*[24] The synthesis involved the reaction of a polydimethylsilane, $[(CH_3)_2Si]_n$, with *B*-trimethyl-*N*-triphenyl borazine, $[CH_3B—NPh]_3$. An organosilicoboron compound was formed by the subsequent thermal treatment of the mixture of both compounds between 250 and 500 °C. The resulting polymer could be melt-spun into fibres[24] and was used as a ceramic binder. The polymeric fibres were cross-linked to infusible products by spinning at 240 °C in air or by electron-beam irradiation and were finally transformed to ceramic fibres with 11 μm diameter by pyrolysis up to 1200 °C in an inert atmosphere. The ceramic fibres irradiated by an electron beam had the composition (wt%) Si 60.5; C 34.7; B 0.91; N 1.18; O 2.71. The tensile strength was measured as 3.2 GPa at room temperature and 2.2 GPa at 1500 °C.

Hydroboration of reactive molecules containing double bonds such as C═C and C═N are an alternative route for the synthesis of boron-containing compounds. The hydroboration of dichloromethylvinylsilane with dimethyl sulphide–borane in toluene led to tris[(dichloromethylsilyl)ethyl]borane (**3**) in high yield (94%).[25] After polycondensation of **3** with ammonia, an organopolyborosilazane **4** with 4 wt% boron content could be isolated (Eqn [4]).[5,8] ^{11}B and ^{29}Si NMR investigations showed that the structure of polymer **4** contains cyclic methylsilazane units $[—R_1R_2Si—NH—]_n$ with $n = 2$, 3 or 4, cross-linked via C–B–C bonds (Fig. 4a). This boron-containing polysilazane **4** could easily be hand-drawn into fibres.[5,8] Pyrolysis under argon at 1100 °C gave Si–B–C–N ceramic fibres without an intermediate cross-linking step (Fig. 4b). The diameter of the ceramic fibres varied between 2 and 30 μm. The resulting Si–B–C–N ceramic was obtained in 62 wt% yield and contained 6 wt% boron. The molar composition was determined to be $SiB_{0.34}C_{1.47}N_{0.68}$ by elemental analysis. The solid-phase density of the amorphous fibres was found to be $2.5\ g\ cm^{-3}$ and is in the range of commercially available polymer-derived silicon-based ceramic fibres.[5]

According to thermogravimetric analysis (TGA) measurements under 0.1 MPa helium and at a heating rate of $5\ K\ min^{-1}$, the thermal degradation of the Si–B–C–N ceramic synthesized at 1100 °C started above 2000 °C. A weight loss of 6 wt% was detected after 2 h of annealing at 2000 °C. This exceptional thermal stability is remarkable in comparison with the behaviour of pure Si_3N_4, which decomposes at temperatures exceeding 1775 °C under 0.1 MPa nitrogen.[9] XRD studies revealed that the ceramic remains amorphous following up to 5 h of isothermal annealing at 1700 °C. Above 1700 °C, a nanocrystalline β-Si_3N_4/β-SiC composite formed.[5]

The boron content in the organopolyborosilazane-derived ceramic could be decreased to 3 wt% by co-ammonolysis of **3** with

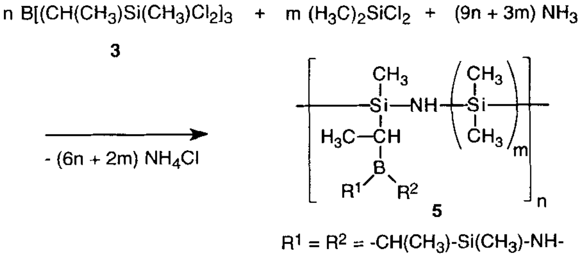


(a)

(b)

Figure 4 (a) Proposed molecular structure of the as-synthesized organopolyborosilazane **4** derived from ^{11}B- and ^{29}Si-NMR investigations.[5] (b) Ceramic fibre (SEM micrograph) of the composition $SiB_{0.34}C_{1.47}N_{0.68}$ synthesized by dry-spinning of the organopolyborosilazane **4** and subsequent pyrolysis of the polymer fibre at 1100 °C under argon (after Ref. 5).

$(CH_3)_2SiCl_2$ followed by pyrolysis of the reaction product, polyborosilazane **5** (Eqn [5]).



$$n\,\underset{\mathbf{3}}{\mathrm{B[(CH(CH_3)Si(CH_3)Cl_2]_3}} + m\,(H_3C)_2SiCl_2 + (9n+3m)\,NH_3 \xrightarrow[-(6n+2m)\,NH_4Cl]{} \underset{\mathbf{5}}{\left[-Si(CH_3)(CH(CH_3)B R^1 R^2)-NH-\left(Si(CH_3)_2\right)_m- \right]_n}$$

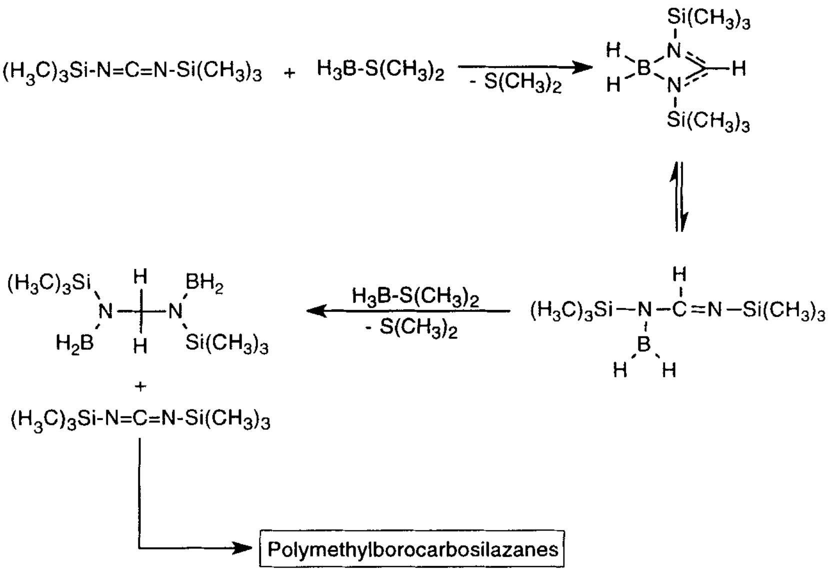
$R^1 = R^2 = -CH(CH_3)-Si(CH_3)-NH-$ [5]

The resulting silicoboron carbonitride, with the molar composition $SiB_{0.17}C_{1.14}N_{0.89}$ and containing 3 wt% boron, exhibited a reduced thermal stability with respect to the material with a boron content of 6 wt%.[5] In this case, β-Si_3N_4 and β-SiC started to crystallize at temperatures exceeding 1600 °C. Furthermore, the thermodynamically favoured reaction of β-Si_3N_4 with excess carbon to β-SiC and elemental N_2 according to Eqn [6] took place under these conditions. Accordingly, a powder pattern that can be assigned to β-SiC was found in the XRD of the material annealed at 1700 °C.

$$Si_3N_4 + 3C \xrightarrow{T>1440\,^\circ C} 3\,SiC + 2N_2 \qquad [6]$$

Boron contents higher than 6 wt% in the resulting ceramic were obtained by the reaction of the organopolyborosilazane **4** with dimethyl sulphide–borane. The boron content could be increased to 14.2 and 16.3 wt%.[5]

Polymeric silylcarbodi-imides $[-R_2Si-N{=}C{=}N-]_n$, represent a new type of precursor suitable for the synthesis of materials in the ternary Si–C–N system.[8,26,27] Moreover, hydrobo-



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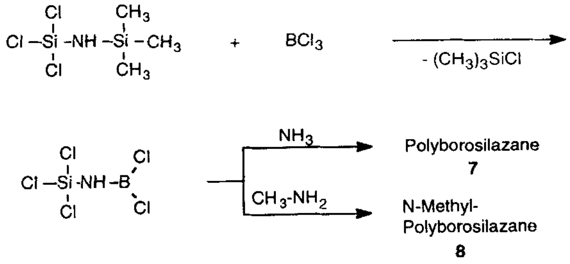
Scheme 1 Synthesis of polymethylborocarbosilazanes.

ration of polysilylcarbodi-imides gave highly cross-linked boron-containing polymners.[5]

The hydroboration of the carbodi-imide unit was monitored by the reaction of bis(trimethylsilyl)carbodi-imide with dimethyl sulphide–borane in toluene (Scheme 1). In a first step, the carbodi-imide unit is hydroborated by 2 mol of borane, whereby the *sp*-carbon atom is reduced to a methylene carbon atom with sp^3-hybridization. Further intermolecular hydroboration of the residual —BH_2 groups with unreacted bis(trimethylsilyl)carbodi-imide results in the formation of polymethylborocarbosilazanes **6**.

The reactivity of the N═C═N group towards the borane compound used is lower than that of the C═C double bond. Thus, higher reaction temperatures have to be applied. The reaction of monomethyl- and monovinyl-substituted silylcarbodi-imide, $[—(H_3C)(H_2C{=}CH)Si—N{=}C{=}N—]_n$, with dimethyl sulphide–borane in toluene immediately started at room temperature. Infrared spectroscopic investigation of the resulting polymer revealed a selective decrease of the C—H vibrations of the vinyl groups indicating that it was mainly the vinyl group that was hydroborated. In contrast, the reaction of the dimethyl-substituted polysilylcarbodi-imide, $[—(H_3C)_2Si—N{=}C{=}N—]_n$, with dimethyl sulphide–borane resulted in extensive cross-linking to form a gel after 24 h reaction time at room temperature. In this case, the IR spectra of the polymer obtained showed a pronounced decrease of the characteristic N═C═N vibration band located at 2210 cm^{-1}. Pyrolysis of the hydroborated methylvinylpolysilylcarbodi-imide at 1100 °C under argon provided a ceramic in 64 wt% yield which was analysed to have the empirical formula $SiB_{0.55}C_{2.20}N_{1.85}$ (6.1 wt% boron). The hydroborated polydimethylsilylcarbodi-imide, when pyrolysed at 1200 °C under argon, formed a ceramic with the empirical formula $SiB_{0.7}C_{1.5}N_{1.85}$ (9.3 wt% boron content).

The synthesis of polyborosilazanes was also described by Baldus *et al.*[28a] Ammonolysis of (trichlorosilylamino)dichloroborane (TADB) with liquid ammonia at −78 °C for four days provided an insoluble white solid (Scheme 2).



Scheme 2 Synthesis, ammonolysis and aminolysis of TADB.

After thermal decomposition of the synthesized polymer **7** under a stream of ammonia at 1000 °C for 24 h and subsequent annealing of the product at 1450 °C in nitrogen, a ceramic with the stoichiometry $Si_3B_3N_7$ was obtained. X-ray powder diffraction of the product annealed in nitrogen revealed that the silicoboron nitride crystallizes at 1750 °C. Thermal degradation of $Si_3B_3N_7$ powder ($60\,m^2\,g^{-1}$) in a helium atmosphere started at temperatures exceeding 1550 °C and the weight loss determined at 1800 °C was 35 wt%. Silicon, boron nitride and elemental nitrogen were formed as the decomposition products.

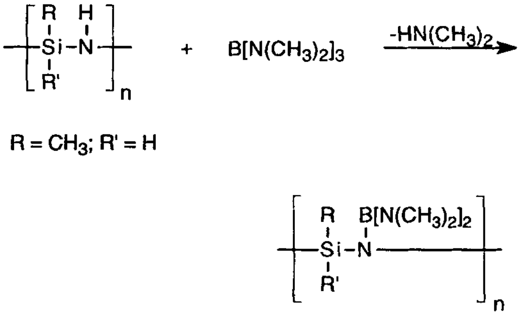
Aminolysis of TADB with methylamine at −20 °C resulted in the formation of a yellow solid **8** with a softening point of about 130 °C[28a] as shown in Scheme 2. The soluble and meltable *N*-methylpolyborosilazane **8** is obtained with an average molecular weight M_w of $2500\,g\,mol^{-1}$, in about 80 wt% yield.[28b] This polymer could be spun into fibres either by melt- or dry-spinning.[28c] Pyrolysis under an inert gas atmosphere led to amorphous black silicoboron carbonitride fibres in 70 wt% yield and with the molar composition $SiBN_3C$. This quaternary ceramic was reported to exhibit a 10-fold improved oxidation resistance compared with Si_3N_4 and SiC, as determined by the measurement of the respective parabolic rate constants.[28c] Moreover, the $SiBN_3C$ was characterized by an extraordinarily high thermal stability up to 2000 °C in helium or nitrogen. The material retained the amorphous state up to 1800 °C in argon and up to 1900 °C under nitrogen.[28c]

Recently, Löffelholz and Jansen reported on the synthesis of polyborosilazanes by the reaction of tetrakis(methylamino)silane with a Lewis-base adduct of borane such as $BH_3 \cdot N(C_2H_5)_3$ according to Eqn [7].[29] Pyrolysis of the as-synthesized polymethylborosilazane **9** was conducted in a dry ammonia stream at 1000 °C, with an annealing time of 12 h at this temperature. The ceramic products were finally calcined for 6 h at 1500 °C in nitrogen. As the reaction product, a colourless and X-ray-amorphous powder with the composition $Si_3B_3N_7$ was obtained in 60–70 wt% yield.[29]

$$n\,Si(NHCH_3)_4 + nBH_3 \xrightarrow{\text{toluene/N(C}_2\text{H}_5\text{)/reflux}} [\!-\!NCH_3\!-\!Si(NHCH_3)_2\!-\!NCH_3\!-\!BH\!-\!]_n + 2n\,H_2 \quad [7]$$

The material revealed no crystallization, even after heat treatment at 1500 °C for 72 h.

The reaction of polyhydridomethylsilazanes of the form $[\!-\!(CH_3)_2Si\!-\!NH\!-\!]_m$ $[CH_3SiH\!-\!NH\!-\!]_n$ with tris(dimethylamino)borane in xylene solvent gave boron-doped organosilicon polymers.[30] Heating the reaction mixture reflux for 340 h resulted in the formation of boron-doped polyhydridomethylsilazane **10** by transamination (Eqn [8]). Further intermolecular transamination of **10** formed polyhydridomethylsilazanes cross-linked via N–B–N bridges.



10 [8]

The thermally induced polymer-to-ceramic conversion of the boron-doped polyhydridomethylsilazane **10** was accomplished under flowing argon at 1000 °C and with an isothermal hold for 4 h at the final temperature. This procedure provided a ceramic containing 1.1 wt% boron in 74 wt% yield with the empirical formula $SiB_{0.054}C_{0.65}N_{1.06}$ calculated from elemental bulk analysis.[30a]

Materials in the quaternary system Si–B–N–O

The synthesis of materials in the quaternary system Si–B–N–O reported in 1993 by Funayama *et al.* was accomplished by the reaction of perhydropolysilazane, $[\!-\!H_2Si\!-\!NH\!-\!]_n$, with trimethoxyborane, $B(OCH_3)_3$, in pyridine as the solvent.[31] The starting polymer, perhydropolysilazane, was synthesized by reacting the $H_2SiCl_2 \cdot$ pyridine adduct with ammonia (Eqn [9]).[32]

$$n\,H_2SiCl_2 \cdot 2C_5H_5N + 3nNH_3 \rightarrow [\!-\!H_2Si\!-\!NH\!-\!]_n + 2n\,NH_4Cl/C_5H_5N \cdot HCl \quad [9]$$

The isolated reaction product, a perhydrosilazane oligomer, was subsequently polymerized by heat-treating the oligomer, dissolved in pyridine, in the presence of ammonia at 90 °C for 16 h in an autoclave. This synthesis procedure provides perhydropolysilazane with a number-average molecular weight M_n of about 2800 g mol^{-1}. The proposed molecular structure of perhydropolysilazane is given in Fig. 5.[33]

According to spectroscopic studies (Fourier transform IR and NMR) the reaction of perhydropolysilazane with trimethoxyborane results in the formation of B—N bonds following Eqn [10] rather than the reaction of the borane at the silicon atom forming Si—O—B bonds according to Eqn [11].

$$[\text{—H}_2\text{Si—NH—}]_n + (\text{CH}_3\text{O})_3\text{B} \rightarrow [\text{—H}_2\text{Si—N(B(OCH}_3)_2)\text{—}]_n + \text{CH}_3\text{OH} \qquad [10]$$

$$[\text{—H}_2\text{Si—NH—}]_n + (\text{CH}_3\text{O})_3\text{B} \rightarrow [\text{—HSi(O—B(OCH}_3)_2)\text{—NH—}]_n + \text{CH}_4 \qquad [11]$$

The O/B atomic ratio in the synthesized polyborosilazane was determined by elemental analysis to be 1.09, indicating that the polymer predominantly contains $=\text{N—B(OCH}_3)\text{—N}=$ units. Further structural units that could be spectroscopically identified are (1) $HSiN_3$, (2) H_2SiN_2 and (3) $HSiON_2$.

The thermally induced conversion of the polyborosilazane in an ammonia stream starts at $T >$ 100 °C and is complete at $T = 800$ °C. The weight loss up to 200 °C is 10% and is due to evaporation of residual solvent (pyridine). The thermal degradation of the polymer on heating between 200 and 800 °C (5 °C mn^{-1}) takes place at a nearly constant rate and results in a mass loss of 10 wt% according TGA measurements. The gaseous species evolved during the polymer pyrolysis include hydrogen, hydrocarbons and silicon-containing volatiles.[31] Detailed gas-chromatographic analysis showed that between 200 and 1000 °C H_2 is evolved, whereas between 400 and 800 °C CH_4 is released.[34]

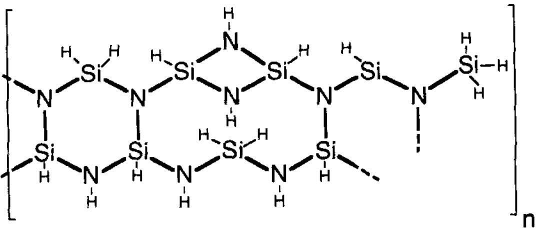


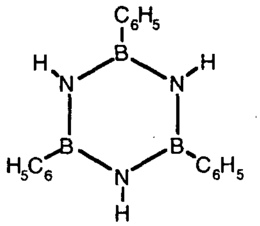
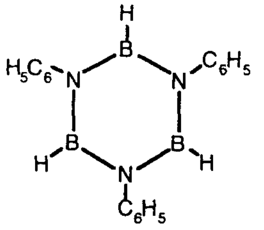
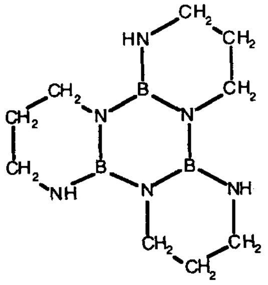
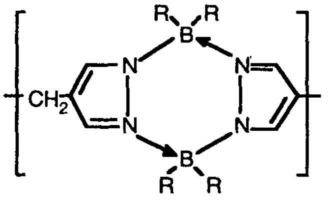
Figure 5 Proposed structure of perhydropolysilazane, the starting polymer for the synthesis of polyborosilazane as precursor for Si-B-N-O ceramics (after Ref. 33).

The thermal stability of the resulting Si—B—N—O ceramic was studied by TGA experiments from 1000 °C up to 1700 °C in nitrogen. Accordingly, the samples pretreated under ammonia to 1000 °C revealed no weight change up to 1700 °C. In contrast, the mass of boron-free perhydropolysilazane-derived Si_3N_4 ceramic decreased by about 20 wt% above 1500 °C owing to the loss of SiO and to the decomposition of silicon nitride.[31] These findings indicate that the presence of boron inhibits the formation of volatile SiO and the decomposition reaction. This is an important result with respect to the synthesis of novel high-temperature-resistant ceramic materials based on silicon nitride.

The high thermal stability of the silicoboron oxynitride is also demonstrated by comparison of the elemental analysis of the material obtained after synthesis at 1000 °C in ammonia and after subsequent annealing of the product at 1700 °C in nitrogen. Accordingly, the silicoboron oxynitride is characterized by the empirical composition $Si_{3.0}B_{1.0}N_{3.9}O_{1.0}$, which remains nearly constant in the temperature range between 1000 and 1700 °C. Infrared investigations revealed the presence of B-O, B-N and Si-N bonds in the polyborosilazane-derived ceramic, while X-ray photoelectron spectroscopy (XPS) analysis also showed that Si-O bonds formed in the sample annealed at 1700 °C in nitrogen. XRD and TEM analysis support an amorphous structure up to 1700 °C.[31,35] After heat-treatment of the silicoboron oxynitride at 1800 °C under nitrogen, a mass loss of 23 wt% was detected together with the formation of α-Si_3N_4 and β-Si_3N_4 as crystalline phases. However, the nature of the residual boron content has not been clear until now, since BN could not be detected by XRD analysis. One explanation discussed is that BN forms substitutional solid solutions with α-Si_3N_4.[31] In summary, the boron atoms suppress the crystallization of silicon nitride and stabilize the amorphous phase.

The polyborosilazane could be dry-spun after removing insoluble material and after developing an appropriate viscosity by concentrating the polymer solution.[35] Continuous polymer fibres with diameters of 10–15 μm were obtained at a spinning temperature of 60 °C. The polymer fibres were pyrolyzed in flowing anhydrous

Table 1 Precursors for the synthesis of boron carbonitrides, $B_xC_yN_z$

Precursor	Formula	product	Ref.
B-triphenylborazine		$BC_{3.9}N$	47
N-triphenylborazine		$BC_{3.6}N$	47
Decaborane(12)-adducts of diamines	$[\text{—}B_{10}H_{12}\cdot\text{diamine—}]_n$	$B_xC_yN_z$	48–50
Piperazine–borane	$BH_3 \cdot C_4H_{10}N_2$	BC_2N	51
Pyridine–borane	$BH_3 \cdot C_5H_6N$	B_4C/BC_4N	51, 52
Dodecahydrotris([1,3,2]diazaborino [1,2-*a*: 1′,2′-*c*: 1″,2″-*e*])borazine		$B_xC_yN_z$	53
Polymeric cyanoborane	$[CNBH_2]_n$	$B_xC_yN_z$	54
Pyroazabole polymer		$B_xC_yN_z$	55, 56
Polyethyleneiminoborane	$[\text{—}CH_2\text{—}CH_2\text{—}N{=}BH_2\text{—}]_n$	$B_xC_yN_z$	57

ammonia with a heating rate of 5 °C min^{-1} up to 1200 °C and subsequent annealing for 1 h under flowing nitrogen at temperatures between 1300 and 1800 °C. The Si–B–N–O fibres heat-treated at 1500 °C exhibited a density of 2.40 g cm^{-3}. The maximum mechanical properties were measured with fibres 8–12 μm in diameter and annealed at 1600 °C. The tensile strength and the Young's modulus were determined to be 2.5 GPa and 180 GPa, respectively.[35] At higher annealing temperatures the mechanical properties significantly decrease due to crystallization of the amorphous matrix.

TERNARY AND QUATERNARY BORON CARBIDE/NITRIDE CERAMICS

Materials in the ternary system B–C–N

Because the C_2 and BN units are isoelectronic and BN and graphite have similar crystal structures, several attempts have been made during the last few decades to prepare solid solutions of these two materials. Boron carbonitrides, $B_xC_yN_z$, are graphite-like materials that exhibit high thermal shock and chemical resistance, as well as interesting electrical properties.[36]

Boron carbonitrides can be obtained from the elements at temperatures around 2000 °C.[37, 38] Moreover, these materials have been prepared by chemical vapour deposition (CVD) processes. In this context, Badzian *et al.* prepared these graphite-like materials by the reaction of gaseous mixtures of BCl_3, CCl_4, N_2 and H_2 at 1900 °C (Eqn [12]).

$$BCl_3 + CCl_4 + N_2 + H_2 \xrightarrow{1900\,°C} (BN)_xC_{1-x} \qquad [12]$$

Heat-treatment of this material at 3300 K and 14 GPa results in the formation of ternary mixed crystals of diamond and cubic boron nitride.[40]

On the basis of this work, Bartlett and coworkers synthesized B_2CN_2,[41] $B_{0.485}C_{0.03}N_{0.485}$ and $B_{0.35}C_{0.3}N_{0.35}$[42] by the reaction of boron trichloride with acetylene and ammonia (Eqn [13]). If acetonitrile is used, a material with the composition BC_2N is obtained (Eqn [14])[43]

$$BCl_3 + yC_2H_2 + zNH_3 \xrightarrow[-HCl]{700\text{–}800\,°C} B_xC_yN_z \qquad [13]$$

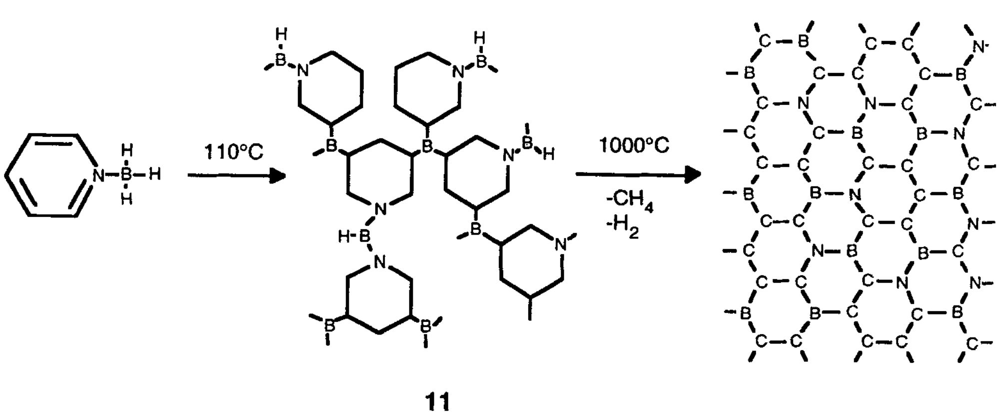
$$BCl_3 + CH_3CN \xrightarrow{800\,°C} BC_2N \times 3HCl \qquad [14]$$

The materials consist of a turbostratic layered structure that contains sp^2-hybridized B, C and N atoms according to XRD and TEM studies. XPS investigations of $B_{0.485}C_{0.03}N_{0.485}$ and $B_{0.35}C_{0.3}N_{0.35}$ reveal the presence of C–C, B–N, C–N and B–C bonds. The semiconducting properties of $B_{0.35}C_{0.3}N_{0.35}$ and BC_2N were detected by electrical measurements.

Instead of C_2H_2, other hydrocarbons such as CH_4 and C_3H_8 have been used for the preparation of these ternary phases.[44, 45] Besmann obtained single-phase $BC_{0.43}N_{0.29}$ with a graphite-like structure from BCl_3–NH_3–CH_4–H_2 mixtures at 1650 K and 3.3 kPa.[46]

In contrast to the CVD method of preparing ternary $B_xC_yN_z$ materials, the pyrolysis of polymeric precursor materials can be used to synthesize the same materials at relatively low temperatures around 1000 °C in high yields. Table 1 provides an overview of different boron-containing precursors suitable for the synthesis of ceramics in the ternary B–C–N system.

Lechner examined the decomposition of amine–boranes such as t-butylamine–, trimethylamine– and dimethylamine–borane in an autoclave at 1000 °C. Thermal treatment of *B*-triphenylborazine and *N*-triphenylborazine under the same conditions yielded the boron carbonitrides $BNC_{3.9}$ and $BNC_{3.6}$, respectively.[47]



11

Scheme 3 Decomposition of pyridine–borane into turbostratic graphite-like boron carbonitride.

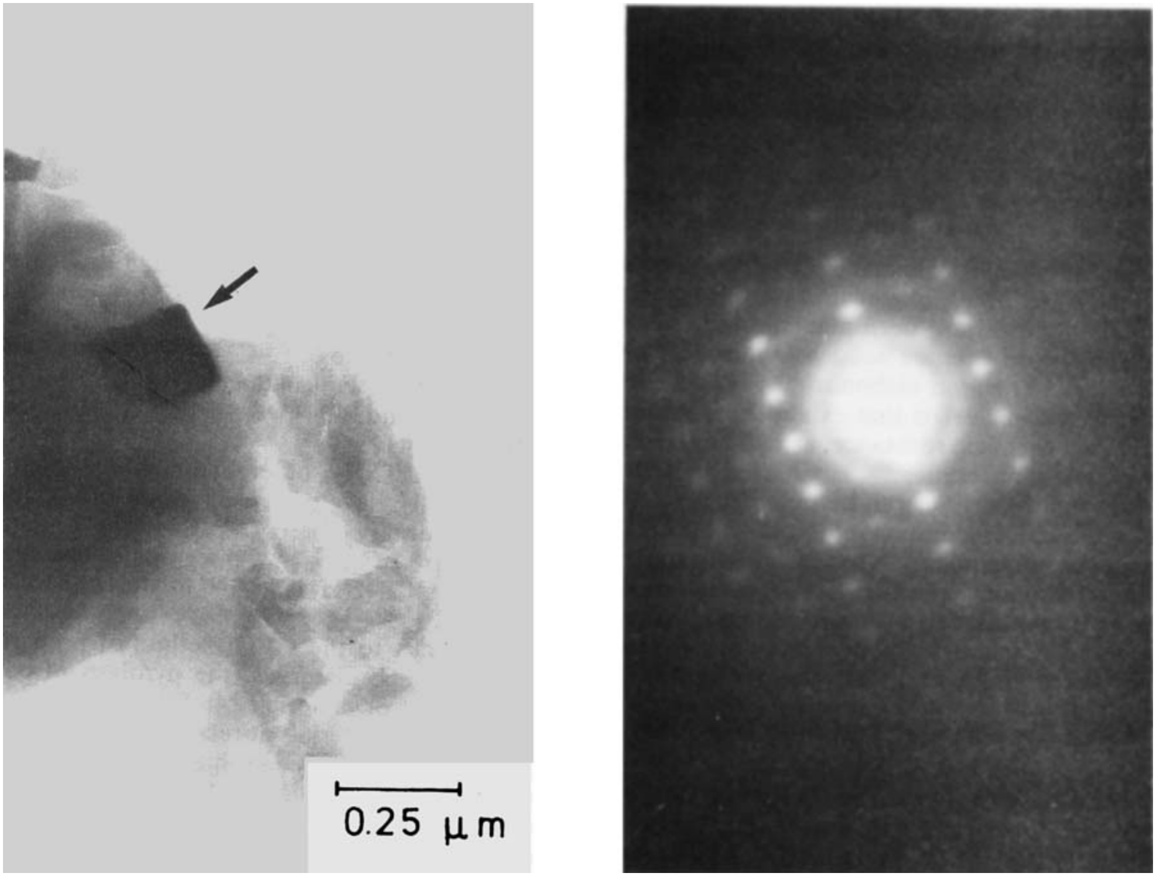
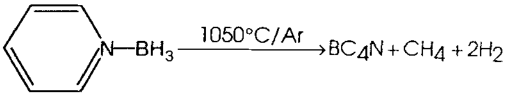


Figure 6 (a) Bright-field image in TEM mode (left) and the corresponding electron diffraction pattern (right) of a crystallite (see arrow) found in the pyrolysis product of pyridine–borane.[58,62]

Seyferth and coworkers prepared boron carbonitride by pyrolysis of polymers $[\text{—}B_{10}H_{12}\cdot\text{diamine—}]_n$ at 1000 °C. Annealing of the material at 1500 °C resulted in the crystallization of α-BN and B_4C.[48–50]

Amine–boranes such as pyridine–borane can also be used for the synthesis of polymers that can be converted into boron carbonitrides,[58–63] while aliphatic amine–boranes such as dimethylamine–borane evaporate during the pyrolysis step; amine–boranes such as pyridine–borane or piperazine–borane transform into polymers which can be converted into boron carbonitride via solid-state pyrolysis. In the case of pyridine–borane, the boron-containing polymer **11** is obtained at 110 °C in an inert atmosphere (Scheme 3). Thermal decomposition of the organoboron polymer **11** at 1000 °C under argon yields semiconducting boron carbonitride with a BC_4N empirical composition and a graphite-like turbostratic structure.[64] TEM, electron spectroscopy for chemical analysis (ESCA) and solid-state NMR investigations reveal the presence of a single-phase matrix material with a homogeneous distribution of the elements. In the graphite sheet structure on the right of Scheme 3, only the sp^2 σ bonds are shown. Equation [15] represents the overall decomposition reaction.



[15]

Besides the single-phase matrix, small amounts (less than 1 wt% as estimated by TEM investigations) of a crystalline phase can be detected by electron microscopy and electron diffraction. Figure 6(a) shows a TEM bright-field image of

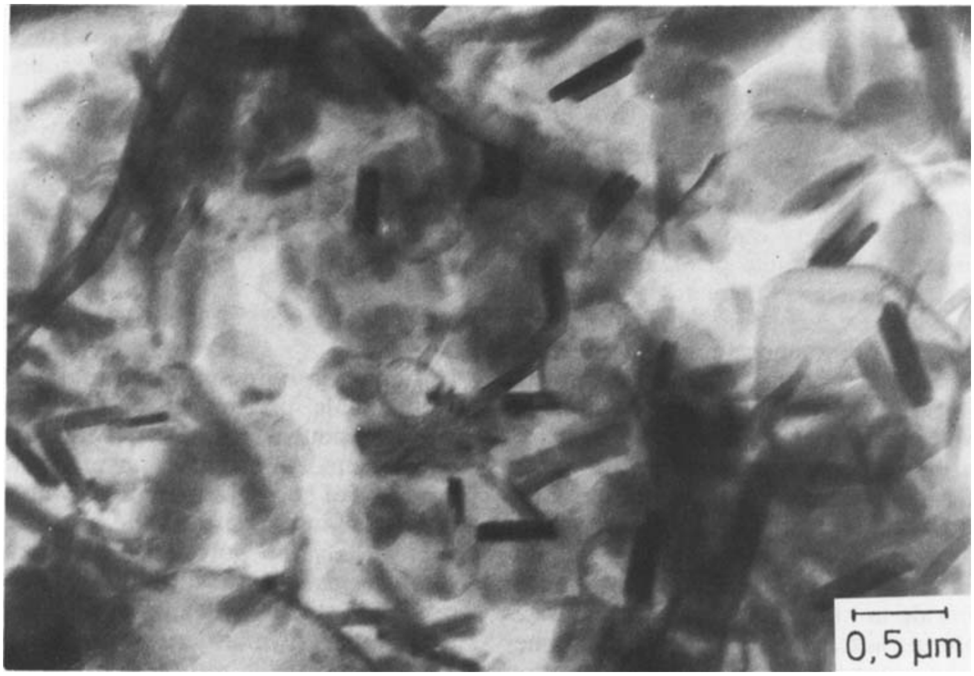
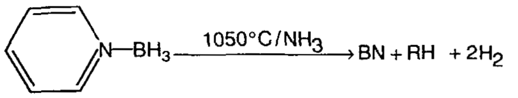


Figure 6 (b) TEM-Bright-field image of a polycrystalline area found in the pyrolysis product of pyridine–borane after heat treatment at 1800 °C and 190 MPa.[58]

this phase with the corresponding electron diffraction pattern. Additionally, polycrystalline areas are found to be formed. Electron diffraction of these areas reveals that the crystallites consist of a face-centered cubic structure. The nature of these crystals, pure diamond, cubic BN or cubic $B_xC_yN_z$ solid solutions, is presently under investigation.

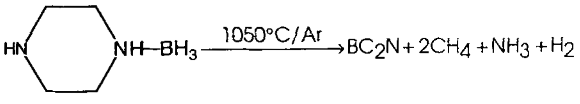
After heat-treatment of the as-synthesized BC_4N at 1800 °C and 190 MPa argon pressure, whisker-like crystals are found in the microstructure [Fig. 6(b)]. The lattice parameters determined by electron diffraction in the TEM mode are in accordance with those of α-BN and graphite indicating partitioning of the BC_4N phase.

If the polymer-to-ceramic transformation is carried out under an ammonia atmosphere, carbon is burnt out completely and BN with a layered structure is formed (Eqn [16]).



[16]

Pyrolysis of piperazine–borane under an inert atmosphere yields boron carbonitride with the composition BC_2N (Eqn [17]).



[17]

The pyridine- and piperazine–borane-derived polymers can be converted into nearly dense BC_4N and BC_2N bulk materials by milling, sieving, shaping and subsequent pyrolysis by hybrid-processing (Fig. 2).

Increasing the temperature above 1800 °C transforms the boron carbonitrides into $B_4C/BN/C$ composites as Eqn [18] depicts for BC_4N.

$$BC_4N \xrightarrow{\text{Ar, 2200 °C}} 0.068B_4C + 0.729BN + 3.932C + 0.136N_2 \qquad [18]$$

This phase-partitioning of the BC_4N matrix analysed by X-ray powder diffraction agrees well with thermodynamic calculations.[60]

Materials in the ternary and quaternary systems Ti–B–N and Ti–B–C–N

Ceramics in the ternary and quaternary systems Ti-B-(C)-N are candidate materials with ultra-high hardness and are, therefore, of great fundamental and technological interest with respect to the development of advanced cutting tools.

Materials in the ternary system Ti-B-N can be obtained by coating titanium powder with polyborazylene, $(B_3N_3H_4)_x$.[65] Shaping of the coated powder by cold isostatic pressing and subsequent heat-treatment up to temperatures between 1200 and 1450 °C resulted in the formation of monolithic TiN/TiB_2 composites. Measurement of the composite hardness gave values up to 2.3 GPa.

The pyrolysis of pyridine–borane in the presence of titanium powder can be used for the preparation of ceramics in the quaternary system Ti–B–C–N. Accordingly, nearly-dense monolithic materials made of titanium carbonitride and titanium boride are obtained without pressurization or sintering aids.[62] Figure 7 summarizes schematically the processing steps for the fabrication of the Ti–B–C–N composites. According to this process, uncompacted titanium powder with an average grain size of 80 μm is infiltrated or coated with pyridine–borane in a quartz tube using ultrasound. After annealing at 120 °C for 5 h and subsequent pyrolysis at 1050 °C, a composite made of titanium carbonitride and titanium boride containing excess titanium and boron carbonitride is obtained. At 1500 °C, a solid-state reaction between the excess titanium and boron carbonitride takes place and a monolithic composite material made of titanium carbonitride, TiC_xN_y, and titanium boride, TiB, is formed. The microhardness of the crystallized composite was found to be 20 GPa.[62]

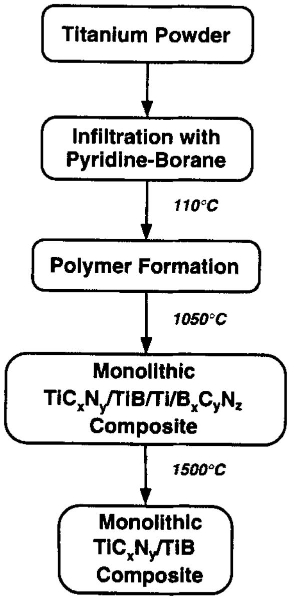


Figure 7 Flow diagram for the synthesis of TiC_xN_y/TiB composites (after Ref. 62).

CONCLUSIONS AND OUTLOOK

In summary, boron-modified inorganic polymers are suitable precursors for the production of multicomponent ceramics with boron as a constituent. A variety of novel methods for the synthesis of boron-containing polymers have been developed in the past decade.

However, the polymer-to-ceramic conversion mechanisms which lead to the final solid are still not understood in detail. Moreover, the structures of the polymer-derived ceramics are also not known, especially in the case of amorphous products. Therefore, future research should focus on (1) the study of the pyrolysis mechanisms, and (2) structural characterization of the final products using different types of model compounds with well-defined structural units.

Furthermore, the processing of novel polymers into multiphase ceramic powders, dense bulk ceramics, fibres, coatings, membranes etc., and their characterization in terms of chemical, mechanical and physical properties, especially at high temperatures ($T > 1000$ °C), are other important tasks. The complexity of the polymer-to-ceramic conversion route requires comprehensive interactions between chemists, physicists and materials scientists in order to understand the basic mechanisms associated with the process and to correlate the materials properties of the final ceramics with the molecular structure of the polymeric precursor.

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