

Si–B–C–N Ceramic Precursors Derived from Dichlorodivynylsilane and Chlorotrivinylsilane. 2. Ceramization of Polymers and High-Temperature Behavior of Ceramic Materials

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Received April 4, 2002

Starting from five different Si–B–C–N polymeric precursors with B/N atomic ratios ranging from 1:3 to 1:0.5, ceramic materials were synthesized by thermolysis at 1400 °C in about 70–75% yield. During this transformation, the Si/B/N ratio remained roughly constant, whereas H and C contents were reduced. The crystallization behavior of as-obtained ceramics was studied by X-ray diffraction. SiC was detected as the first crystalline phase forming during thermolysis or subsequent annealing. Further phase evolution can be predicted following thermodynamic calculations depending on the composition which is, for the different as-obtained materials, located in or close to the phase fields BN + Si₃N₄ + C, BN + Si₃N₄ + SiC + C, BN + SiC + C, or BN + B_{4+δ}C + SiC + C. The SiC-poor (Si₃N₄-rich) material was not high-temperature stable and decomposed releasing nitrogen, whereas SiC-rich (Si₃N₄-poor) materials were mass stable up to 2000 °C.

1. Introduction

Precursor-derived ceramic materials based on silicon and including the elements carbon, nitrogen, or boron are usually obtained by thermolysis of highly cross-linked organometallic polymers at temperatures up to 1400 °C without sintering additives.^{1–5} As previously demonstrated for Si–C–N precursors, the elemental composition of the ceramics is mainly influenced by the respective polymer composition.⁶ During thermolysis, an inorganic network is formed and crystallization leads to microstructures composed of the thermodynamically stable phases, Si₃N₄, SiC, Si, or C.

In boron-containing Si–C–N ceramics, the number of stable phases includes further species, namely, BN and B_{4+δ}C. Thermodynamic calculations reveal that the latter compound should only be present in materials with B/N atomic ratios larger than one.⁷ In thermolysis or heat-treatment experiments, the formation of tur-

bostratic layers of a BNC_x phase was observed with a B/N ratio of 1:1 and excess carbon.^{7,8} The atomic structure of this phase was not well-known until now.

The most amazing feature of many Si–B–C–N ceramics derived from precursors is their extraordinary high-temperature stability.^{3–13} The compositions of these materials are located in the four-phase field BN + Si₃N₄ + SiC + C. The resistance of the ceramics against crystallization and decomposition seems to be related to the concentrations of Si₃N₄ (which has to be low)¹⁴ and BN (preferably high)^{15,16} within the materials, but the respective threshold values possibly vary when changing the precursor system. Therefore, it was interesting to investigate “simpler” materials with compositions located in the neighboring three-phase fields BN + SiC + C and BN + Si₃N₄ + C.

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Table 1. Chemical Composition of As-Thermolyzed Ceramic Materials 1c–5c (wt %)

	Si	C	N	B	O	ceramic formula ^a	polymer formula ^a
1c	33.6	37.8	17.4	9.1	1.8	Si ₁₉ C ₄₉ N ₁₉ B ₁₃	Si ₁₉ C ₇₅ N ₁₉ B ₁₂ H ₁₅₅
2c	27.8	39.0	25.0	7.3	0.6	Si ₁₅ C ₄₈ N ₂₇ B ₁₀	Si ₁₅ C ₇₂ N ₂₉ B ₁₀ H ₁₂₁
3c	25.8	47.1	13.6	11.8	1.8	Si ₁₃ C ₅₇ N ₁₄ B ₁₆	Si ₁₃ C ₁₀₁ N ₁₆ B ₁₆ H ₂₁₂
4c	29.4	51.7	7.8	10.4	0.7	Si ₁₅ C ₆₃ N ₈ B ₁₄	Si ₁₅ C ₉₁ N ₈ B ₁₅ H ₁₈₁
5c	25.9	51.1	13.3	9.9	0.4	Si ₁₃ C ₆₀ N ₁₃ B ₁₃	Si ₁₃ C ₈₆ N ₁₃ B ₁₃ H ₁₅₇

^a Oxygen content is neglected.

In this second part of our study, we used five different Si-B-C-N precursors synthesized in the first part¹⁷ which were likely to produce ceramic materials with compositions in four different phase fields within the Si-B-C-N system. Beside ceramization experiments, phase evolution is described and compared to predictions of thermodynamic calculations.

2. Experimental Section

The synthesis of polymers 1–5 which are analyzed in the following is described in the first part of this study.¹⁷ Elemental composition of the precursors is given in Table 1.

Fourier transform infrared spectra were obtained with a Bruker IFS66 spectrometer as KBr pellets. Reference materials (SiC, Si₃N₄, and BN) were purchased from H. C. Starck GmbH & Co. Kg, Germany.

Chemical analysis was performed using a combination of different analysis equipment (ELEMENTAR Vario EL, ELTRA CS 800 C/S Determinator, LECO TC-436 N/O Determinator) and by atom emission spectrometry (ISA JOBIN YVON JY70 Plus). The ceramic samples were powdered in a WC ball mill prior to analysis (except 2c).

Thermogravimetric analysis (TGA) of the polymer-to-ceramic conversion was carried out in a flowing argon atmosphere (100 cm³/min) with Netzsch STA 409 equipment in alumina crucibles (25–1400 °C; heating rate, 5 °C/min). Thermolysis of bulk preceramic material was performed in Al₂O₃ Schlenk tubes in a flowing argon atmosphere (heating rate, 25–1400 °C, 1 °C/min followed by a dwell time of 2 h).

For high-temperature thermogravimetric analysis (HT-TGA) of the as-obtained ceramic samples a Netzsch STA 501 equipment was used in an argon atmosphere (25–2150 °C; heating rates, $T < 1400$ °C, 10 °C/min; $T > 1400$ °C, 5 °C/min) using carbon crucibles. The crystallization of the as-obtained amorphous ceramics was performed in graphite furnaces using graphite crucibles (heating rates, $T < 1400$ °C, 10 °C/min; $T > 1400$ °C, 2 °C/min; dwell time, 5 h) in an argon atmosphere. The X-ray diffraction unit used for structural investigations of the annealed samples was a Siemens D5000/Kristalloflex (Cu K_{α1} radiation), equipped with a position sensitive proportional counter and a quartz primary monochromator. The samples were powdered in a WC ball mill prior to analysis (except 2c).

3. Results and Discussion

3.1. Polymer-to-Ceramic Transformation. Synthesis of the boron-containing polymers 1–5 is described in the first part of this study.¹⁷ Idealized formulas are given below (C₂H₄: CHCH₃ or CH₂CH₂). The elemental composition of the polymers was analyzed and is summarized in Table 1. (For better comparison, the subscript indices in the polymer formula were adapted to the respective silicon index of the ceramic formula.)

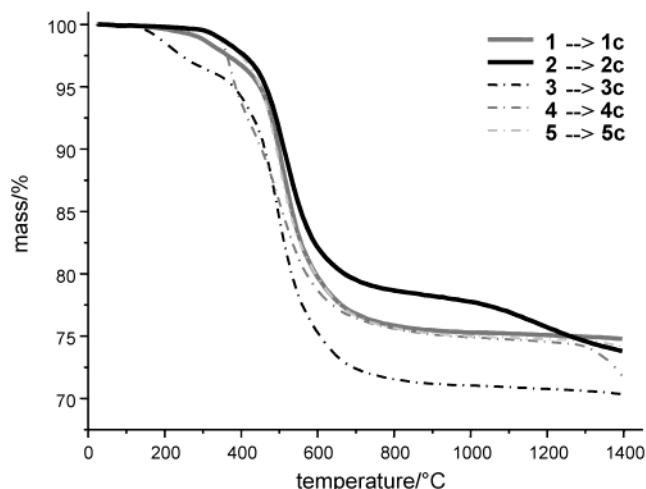
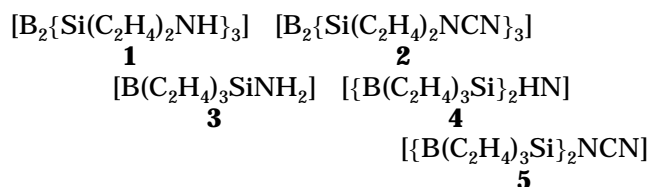


Figure 1. Thermogravimetric analysis of polymers 1–5 (heating rate, 5 °C/min; argon atmosphere).



Polymers 1, 3, and 4 were obtained by hydroboration of silazanes, whereas 2 and 5 are derived from silylcarbodiimides. The important structural units are Si-NH_x-Si_{2-x} ($x = 1, 2$) in the first case, Si-N=C=N-Si in the second case, and BC₃ centers in all polymers. These Si-B-C-N precursors were thermolyzed at 1400 °C in a flowing argon atmosphere to produce black ceramic materials, which in the following discussion are denoted by the polymer number followed by c. The particle size of the ceramics in this study is most probably influenced by the morphology of the respective polymers; materials 1c, 3c, 4c, and 5c, which were obtained by thermolysis of glasslike gels, formed rather compact millimeter-sized grains, whereas thermolysis of fine-grained material 2 delivered a very fine-grained ceramic powder 2c. The approximate grain size of 2c was determined by sieving, whereby 20 wt % of the material consisted of grain agglomerates >80 μm. The size of about 6 wt % was between 80 and 32 μm, and 74 wt % of the as-obtained grains were smaller than 32 μm.

The mass change during the polymer-to-ceramic transformation was detected by thermogravimetric analysis (Figure 1). Polymer 3 exhibits a first mass loss step of about 4% between 140 and 250 °C. This mass loss cannot be caused by evaporation of residual solvent within the polymer because the chemical composition of the material corresponds to the expected polymer formula. Furthermore, chemical analysis revealed that the Si/N atomic ratio of 3 remains almost constant during thermolysis (see Table 1). Therefore, transamination reactions leading to NH₃ formation cannot be important. The observed decomposition up to 250 °C may be attributed to insufficient cross-linking between the monomer units caused by the steric hindrance within the polymer or the inadequate reaction conditions.¹⁷ This may lead to the formation and evaporation of small molecules.

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The most important mass loss for all polymers was detected between 280 and 700 °C in one single reaction step leading to a ceramic yield of 71–78% at 1000 °C.

At temperatures higher than 800 °C, the compositions of the materials **1c**, **3c**, and **5c** remain almost constant. Materials **2c** and **4c** exhibit a second mass loss step which is seemingly not complete at 1400 °C. Decomposition of **2c** is accelerated at temperatures $T > 1000$ °C leading to a mass loss of about 5%. The slope of the curve indicates, though, that the polymer-to-ceramic conversion is almost finished at 1400 °C. This mass loss is probably related to evaporation of $(\text{CN})_2$ or N_2 . The formation of these gases in a similar temperature range was already observed during the thermolysis of different polysilylcarbodiimides.^{18,19}

The second reaction step of material **4c** starts at 1300 °C. Information about further decomposition cannot be deduced from this experiment. However, the approximate final mass loss during bulk thermolysis was determined to be 27%.

The ceramic yields of all of the polymers investigated are comparable and amount to 70–74%. Surprisingly, no qualitative difference was observed between the TGA curves of polyborosilazanes and polyborosilylcarbodiimides up to 1000 °C. The mass losses of materials **1** (derived from oligodivynylsilazane) and **5** (derived from bis(trivinylsilyl)carbodiimide) are even almost identical up to 1400 °C. The similar ceramization progression points out that the chemical reactions involved in the thermolysis of the compounds are very similar.

The compositions of the as-thermolized materials **1c**–**5c** determined by chemical analysis are given in Table 1 and compared to the polymer formulas found by chemical analysis. During thermolysis, the Si/B/N atomic ratios of the materials remain almost constant. The carbon content is significantly reduced by about 31% in materials **2c**, **4c**, and **5c**, by about 35% in **1c**, and by about 44% in **3c**. Hydrogen atoms were not detected in the as-thermolized ceramics (<0.3 wt %).

3.2. High-Temperature Behavior. Phase formation was studied by means of X-ray diffraction (XRD) and infrared (IR) spectroscopy. The as-thermolized ceramic samples were annealed in an argon gas atmosphere for 5 h at different temperatures. Decomposition reactions were additionally investigated by high-temperature thermogravimetric analysis in an argon atmosphere.

X-ray Diffraction. The XRD diagram of as-thermolized material **1c** (see Figure 2) shows very broad reflections which can be attributed to nanometer-sized silicon carbide crystals. Furthermore, two very broad weak signals occurred at about 26 and 43° characteristic for a mixed phase of graphite-like carbon and boron nitride (BNC_x phase). After annealing at 1600 °C, the intensity of these reflections increased without significant signal sharpening. Heat treatment at 1700 °C leads to a noticeable reduction of the half-width of all reflections. The XRD pattern of the 1800 °C sample in Figure 2 shows silicon nitride reflections besides SiC and C signals. Increasing the temperature to 2000 °C did not result in an evolution of further crystalline phases or in a thermal decomposition of the material.

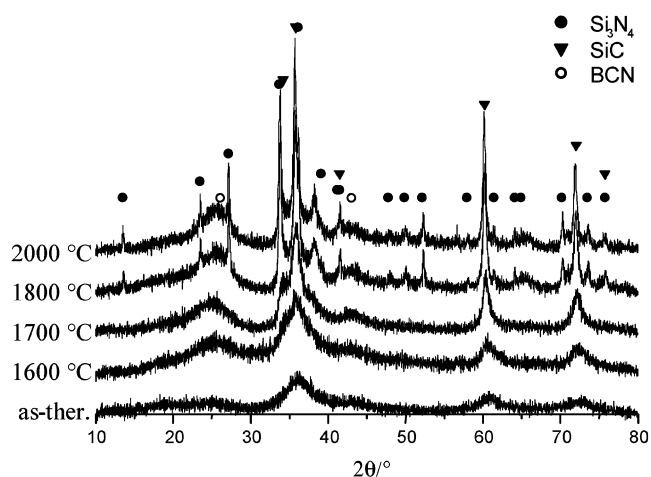


Figure 2. XRD diagrams of as-thermolized and annealed **1c** (dwell time, 5 h; argon atmosphere).

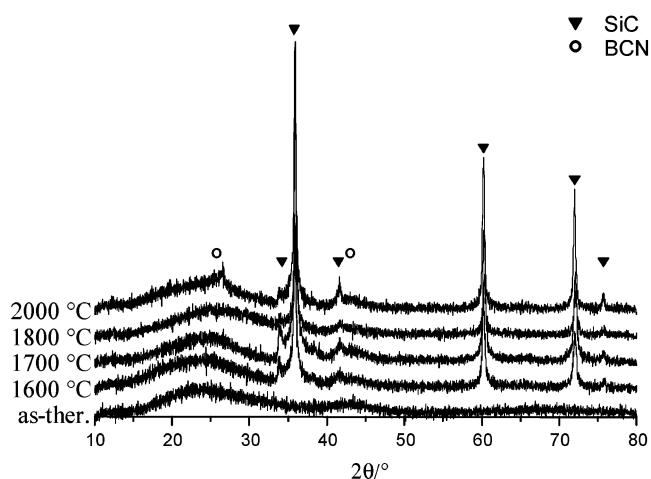
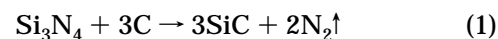


Figure 3. XRD diagrams of as-thermolized and annealed **2c** (dwell time, 5 h; argon atmosphere).

The diffraction diagram of as-thermolized **2c** shows two very broad reflections at about 26 and 42 ° with low intensity that trace back to a BNC_x phase (Figure 3). Crystalline phases which are frequently observed in this type of ceramics were not detected. The sample heat-treated at 1600 °C produces sharp SiC signals besides BNC_x reflections. The formation of SiC at this temperature can be correlated with the thermal degradation of Si–N units of the amorphous phase according to the reaction



which is expected at about 1484 °C.²⁰ Consequently, no crystalline silicon nitride can form at higher temperatures. The sample is predominantly crystalline at 1600 °C. Up to 2000 °C, the diffraction pattern does not change significantly.

The XRD diagrams of the as-thermolized and annealed materials **3c** and **4c** are very similar. In Figure 4 the diagrams of **3c** are shown. In comparison to the diffraction patterns of the ceramics discussed previously, the materials **3c** and **4c** are crystalline to a large extent after thermolysis, showing SiC and BNC_x reflections.

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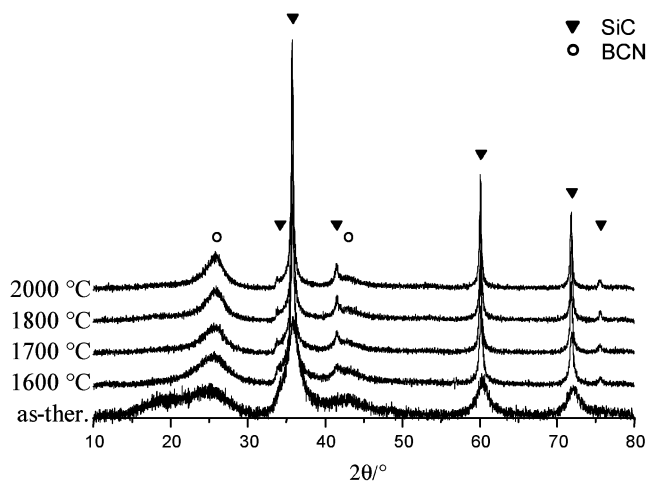


Figure 4. XRD diagrams of as-thermolyzed and annealed **3c** (dwell time, 5 h; argon atmosphere).

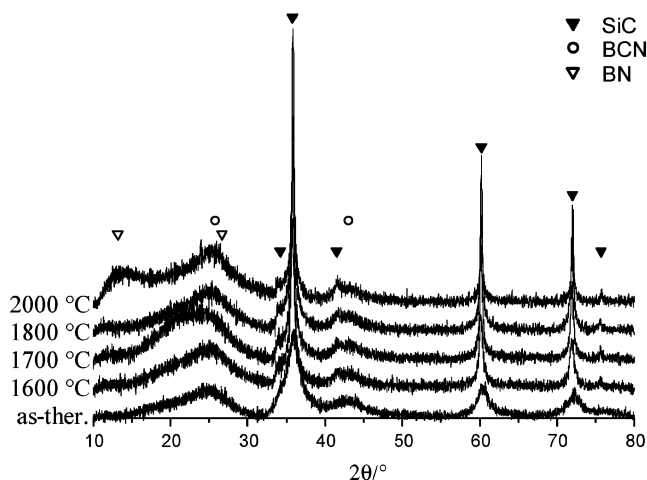


Figure 5. XRD diagrams of as-thermolyzed and annealed **5c** (dwell time, 5 h; argon atmosphere).

The half-width of these signals decreases noticeably at 1600 and 1700 °C. At higher temperatures, crystallization proceeds very slowly. The X-ray patterns of the 1800 and 2000 °C appear almost identical. However, a signal sharpening of the BNC_x reflections was observed. Remarkably, the signals of the BNC_x phase in ceramics derived from silazanes (**1c**, **3c**, **4c**) are always more distinct than those in ceramics derived from silylcarbodiimides (**2c**, **5c**).

The crystallization behavior of material **5c** (Figure 5) resembles that of **3c** and **4c**. An additional broad reflection at about 13° was observed in annealed samples. After the heat treatments at 1600, 1700, and 1800 °C, it is very weak, whereas the intensity increases noticeably in the 2000 °C sample. Most probably, this signal can be assigned to the main reflection peak of hexagonal boron nitride. The possible presence of BN signals in **5c** could be due to the formation of a different microstructure with more ordered layers of BN and C in comparison with **3c**. Investigations using transmission electron microscopy are in progress to examine this phenomenon.

IR Spectroscopy. In Figure 6 the IR spectra of the as-thermolyzed materials, which were obtained in transmission mode, are shown. The positions of the main absorption maxima of crystalline BN, Si_3N_4 , and SiC

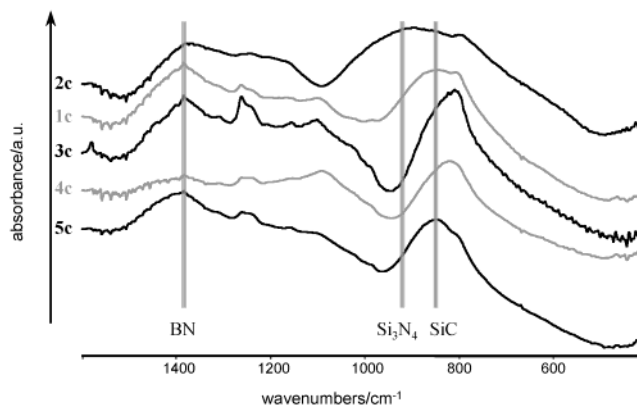


Figure 6. IR spectra (1600–400 cm^{-1}) of as-thermolyzed materials **1c–5c**.

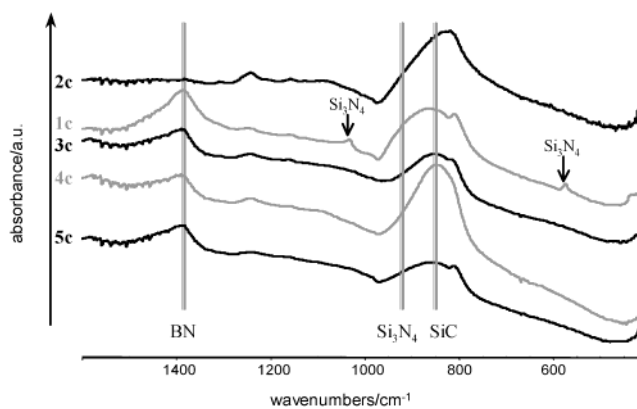


Figure 7. IR spectra (1600–400 cm^{-1}) of annealed materials **1c–5c** (2000 °C, 5 h, argon atmosphere).

are denoted. All spectra show a very broad absorption at about 1380 cm^{-1} characteristic for hexagonal BN. The intensity of this band is significantly smaller in the spectrum of **4c** which has the lowest BN phase fraction.

The spectrum of material **2c** exhibits a broad band between 1100 and 500 cm^{-1} the maximum of which is located at about 900 cm^{-1} . This position approximately corresponds to that of the main absorption of crystalline Si_3N_4 (920 cm^{-1}) with a small bathochromic shift which can be expected in amorphous materials.

The coordination sphere of silicon atoms in materials **3c** and **4c** is clearly dominated by Si–C bonds causing absorption maxima at 810 (**3c**) and 820 cm^{-1} (**4c**). Compared to crystalline SiC (850 cm^{-1}), the shift to lower frequencies can be explained by the partly amorphous character of the materials.

The IR spectra of **1c** and **5c** are very similar. They show a broad band between 950 and 700 cm^{-1} centered at 850 cm^{-1} . Compared to the main absorption of materials **3c** and **4c**, the Si–X (X: C or N) vibration band in **1c** and **5c** is shifted to higher frequencies. This may indicate a larger relative amount of crystalline SiC in these materials. However, the observed band can also be caused by overlapping Si–C and Si–N vibration bands in partly amorphous materials.

The IR spectra of the ceramic materials annealed for 5 h at 2000 °C in an argon atmosphere are shown in Figure 7. The BN vibration band at about 1380 cm^{-1} is still present in all materials except **2c**. Decomposition of boron nitride in **2c** was observed between 1800 and 2000 °C in argon atmosphere; the IR spectrum of the

Table 2. Calculated Relative Phase Fractions (atom %, O Content Is Neglected) of Materials 1c–5c

ceramic	1c	2c	3c	4c	5c	ceramic	1c	2c	3c	4c	5c
BN	26	20	28	16	26	SiC	28	5	27	30	25
B ₄ C ^a	0	0	2	7	0	C	35	46	43	46	48
Si ₃ N ₄	11	29	0	0	1						

^a Simplified formula (see text).

1800 °C sample (not shown here) revealed the presence of BN in the annealed material. Furthermore, BN vibrations were detected in material **2c** after annealing for 3 h at 2000 °C in a nitrogen atmosphere (1 bar). These observations are in accordance with thermodynamic calculations which predict boron nitride decomposition in the presence of carbon at temperatures below 2000 °C if the N₂ pressure is smaller than 0.05 bar^{21,22} (see the following discussion).

The most intensive absorption band in the IR spectrum of material **2c** is centered at 820 cm⁻¹, whereas maximum absorption in crystalline SiC is observed at 850 cm⁻¹. This shift to smaller frequencies is possibly due to partly amorphous SiC structures within the material. In **3c**, **4c**, and **5c**, the position of the Si–C band maximum exactly corresponds to that of crystalline SiC, indicating complete crystallinity of this phase. In material **1c**, this absorption is slightly shifted to higher wavenumbers (865 cm⁻¹) as a consequence of overlapping SiC and Si₃N₄ vibrations. The presence of silicon nitride in this material is also revealed by two bands with low intensity detected at 1032 and 585 cm⁻¹ characteristic for crystalline Si₃N₄.

To better understand the results of the XRD analysis and IR spectroscopy, the chemical compositions of the materials have to be considered and compared to the thermodynamically stable phase compositions. Thermodynamic calculations using the CALPHAD approach (calculation of phase diagrams²³) predict that crystallization of the investigated ceramics leads to the formation of multicomponent materials consisting of boron nitride, boron carbide (B_{4+δ}C), silicon nitride, silicon carbide, or carbon depending on the elemental composition of the as-thermolyzed ceramics which are, in turn, dependent on the polymer composition. Table 2 shows the calculated relative phase fractions of thermodynamically stable phases at 1400 °C and 1 bar N₂ pressure (for simplification, calculations were performed with the formula B₄C instead of B_{4+δ}C). An isothermal section of the Si–B–C–N phase diagram at a constant boron content of 14 atom % was calculated (1 bar N₂, 1400 °C, Figure 8). The compositions of the partly amorphous as-thermolyzed materials **1c** (13 atom % B), **3c** (16 atom % B), **4c** (14 atom % B), and **5c** (13 atom % B) are included. Because of the lower boron content of **2c** (10 atom %), this composition was not inserted. Furthermore, the phase fraction diagrams of **1c**, **2c**, **4c**, and **5c** are shown in Figure 9a–d. The respective diagram of **3c** is omitted because of its similarity to that of **5c**.

The boron/nitrogen atomic ratio in polymers **1** and **2** derived from dichlorodivinylsilane is smaller than 1.

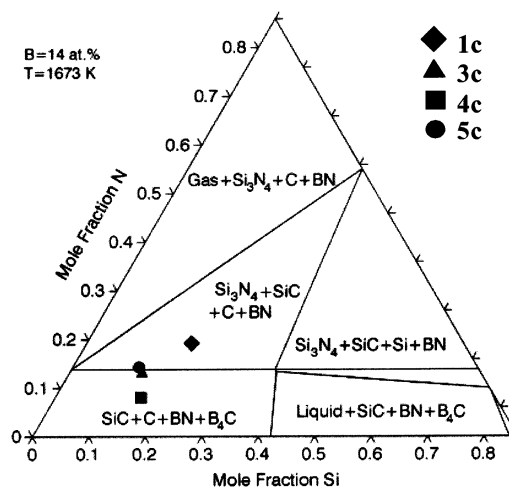
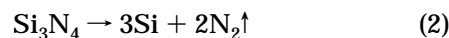
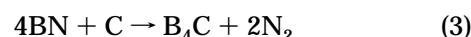


Figure 8. Isothermal section of the Si–B–C–N phase diagram at 14 atom % boron at 1400 °C, 1 bar N₂. The compositions of as-thermolyzed ceramics **1c**, **3c**, **4c**, and **5c** are indicated.

During thermolysis, this ratio remains roughly constant. Hence, the thermodynamically stable phases expected include silicon nitride because nitrogen cannot entirely be bond to boron. Consequently, the composition of material **1c** (◆ in Figure 8) is located in the four-phase field BN + Si₃N₄ + SiC + C. According to thermodynamic calculations (see Figure 9a), complete decomposition of Si₃N₄ by reaction with carbon is expected at 1484 °C (reaction 1). However, reflections of these phases are present in the XRD diagrams of **1c** after annealing at 1800 and 2000 °C, indicating that even Si₃N₄ decomposition into the elements (1840 °C, reaction 2) did not occur. Therefore, it can be concluded that silicon nitride is stabilized in material **1c** as in similar high-temperature stable Si–B–C–N ceramics described in the literature.



In ceramic **2c**, the nitrogen content is highest. The amount of N atoms is slightly smaller than the number of B atoms plus 4/3 of the number of Si atoms. Consequently, only a very small amount of silicon carbide can be present in the as-obtained ceramic. The material is the only one showing no SiC reflections in the as-thermolyzed state. Annealing at 1600 °C initiates the cleavage of Si–N bonds according to reaction 1 with the formation of SiC and simultaneous loss of nitrogen. Therefore, no crystalline silicon nitride can form during heat treatments at elevated temperatures. These observations are in accordance with thermodynamic calculations for this material which predict complete Si₃N₄ decomposition at temperatures higher than 1480 °C (see Figure 9b). Between 1800 and 2000 °C, the BNC_x phase formed during pyrolysis was decomposed in an argon atmosphere, whereas it was stable in a nitrogen atmosphere. Following thermodynamic calculations, the reaction of BN with C should occur at temperatures below 2000 °C at low nitrogen partial pressure (<0.05 bar)^{21,22} (reaction 3).



In polymers derived from chlorotriethylsilane, the boron/nitrogen atomic ratio is equal to or bigger than 1

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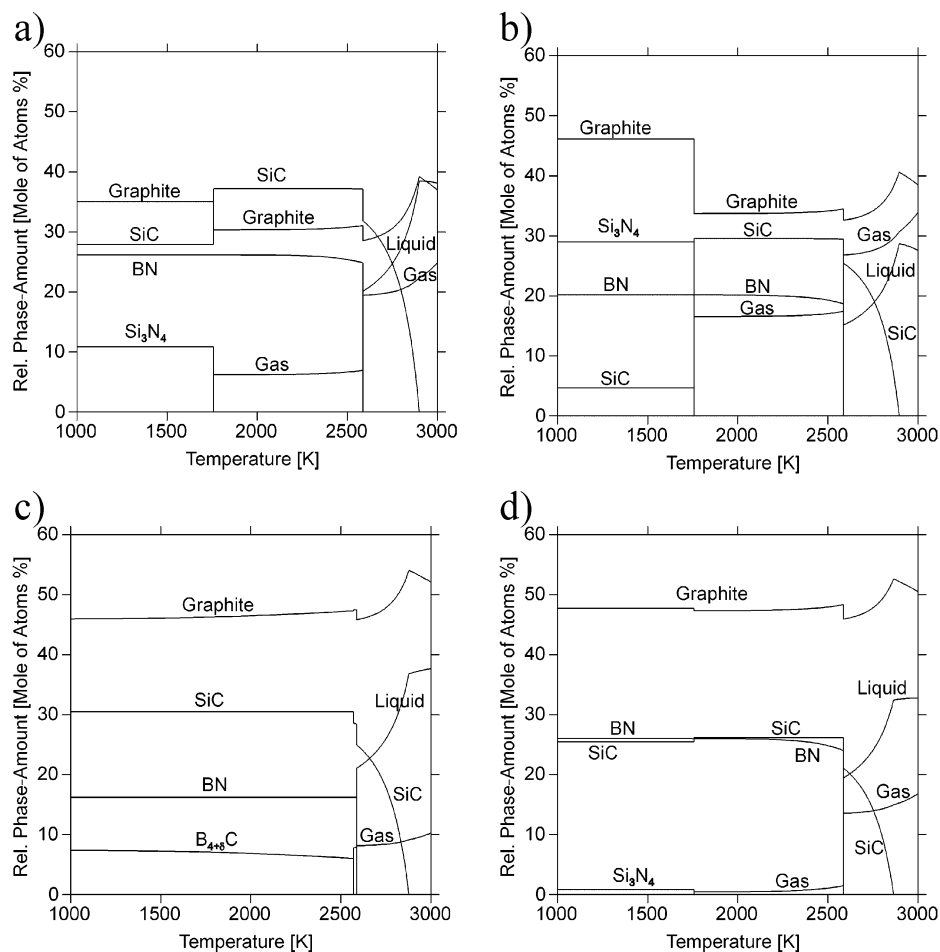


Figure 9. Phase fraction diagrams of as-thermolyzed ceramics (a) **1c**, (b) **2c**, (c) **4c**, (d) **5c**.

and does not change significantly during thermolysis. In the first case ($B/N = 1$), neither Si_3N_4 nor B_4C will form in annealed ceramic samples. The compositions of the materials **3c** (\blacktriangle) in Figure 8) and **5c** (\bullet) in Figure 8) lie in (or very close to) the three-phase field $BN + SiC + C$. Crystalline silicon carbide and a BNC_x phase are already produced during thermolysis. Further crystallization at higher temperatures leads to the formation of a composite material of BNC_x and SiC , thus confirming thermodynamic calculations which predict thermal stability of these materials at temperatures up to 2300 °C (see Figure 9d). Further increase of the temperature should lead to the formation of a gaseous and a liquid phase.

Because of the low nitrogen content in **4c** ($B/N > 1$) a second boron containing phase ($B_{4+x}C$) is expected beside BN , SiC , and C (\blacksquare) in Figure 8). X-ray diffraction experiments revealed the presence of SiC and a BNC_x phase in the as-thermolyzed state. Reflections of boron carbide are absent which might possibly be due to the lacking crystallization tendency of $B-C$ containing phases or the small amount of B_4C expected in this material. The calculated thermal mass stability of this material is illustrated in Figure 9c. According to the phase fraction diagram, the composition of crystallized **4c** should remain constant up to 2300 °C. At higher temperatures, boron carbide is expected to react with silicon carbide to form carbon and a liquid phase. At about 2315 °C, residual SiC and C should react with BN with formation of a gaseous and a liquid phase.

The thermodynamic calculations depicted in Figures 8 and 9 are only valid for 1 bar N_2 atmosphere. Heat-treatment experiments, however, were performed in an argon atmosphere. Therefore, decomposition of the BNC_x phase according to reaction 3 is to be expected for all of the ceramic materials investigated here. Nevertheless, it was only observed by means of IR spectroscopy of material **2c**, whereas the compositions of **1c**, **3c**, **4c**, and **5c** remained constant during the heat treatment. Obviously, the decomposition of BN is effectively retarded in these materials. However, the small weight loss detected at temperatures higher than 2000 °C in the HT-TGA experiments (see the following discussion) is probably related to nitrogen evaporation according to reaction 3.

HT-TGA. To analyze the high-temperature mass stability of the ceramic materials, thermogravimetric analysis was performed in an argon atmosphere up to 2150 °C. The results are shown in Figure 10.

Material **2c**, which is derived from a relatively boron-poor poly(silylcarbodiimide) and which has the highest N content among the materials investigated here, starts to decompose at 1400 °C. The mass loss at 1820 °C amounts to 15%. Further decomposition is retarded and occurs in a second step between 1900 and 2150 °C. The final mass loss at 2150 °C is 21%.

The ceramic **1c** is stable up to 1800 °C. At higher temperatures, decomposition starts slowly and results in a mass loss of 1.6% at 2000 °C and 3.4% at 2150 °C.

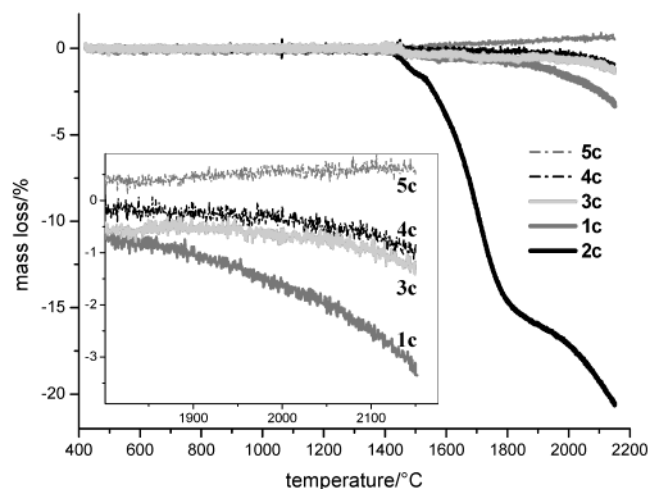


Figure 10. HT-TGA of as-thermolyzed ceramics **1c**–**5c** (400–2150 °C, argon atmosphere; heating rate, $T < 1400$ °C, 10 °C/min; $T > 1400$ °C, 5 °C/min).

The mass changes of the boron-rich materials **3c**–**5c** are very small during the experiments. Whereas the mass losses of **3c** and **4c** are very similar (0.7% and 0.3% at 2000 °C, 1.3% and 1.0% at 2150 °C, respectively), material **5c** has gained 0.6% of its original mass at 2150 °C. These differences are difficult to interpret because they are in the range of experimental error.

These results are in good accordance with the phase compositions calculated from thermodynamic data (see Table 2 and Figures 8 and 9) and XRD investigations. Considering thermodynamic calculations, the as-thermolyzed materials should be composed of BN, $B_{4+\delta}C$, Si_3N_4 , SiC, or C. These phases are all stable at high temperatures exceeding 2000 °C (1 bar N_2) except Si_3N_4 which is the critical compound relating to this. However, the temporary mass stability of material **1c** indicates that silicon nitride can efficiently be protected against decomposition (see reactions 1 and 2) at temperatures up to 2000 °C, even in an argon atmosphere.

The mass loss of material **2c** is related to nitrogen evaporation. The reaction of Si–N units with C is not hindered. This may be due to the fact that the relative amounts of Si_3N_4 and C are larger than in **1c**. The Si_3N_4 /BN phase fractions ratio, however, which is discussed as a decisive number with respect to high-temperature stability, is similar in **2c** and a number of thermally stable materials.^{15,16,22} More likely, the missing cohesion of the material which affects the morphology (fine-grained powder) is responsible for the instability of this material at high temperatures because the evaporation rate depends on the surface area. However, in preliminary HT-TGA experiments performed with bulk ceramic particles **2c**, which were obtained by thermolysis of warm pressed dense glassy **2**, it could be shown that the mass loss is only slightly affected by the particle

size in this material. The phase fraction diagram (see Figure 9b) indicates that Si_3N_4 decomposition should lead to a mass reduction of 16% and the degradation of BN (observable in an argon atmosphere) to a second mass loss of 9%. So, the first reaction step observed in the HT-TGA (–15%) of **2c** can be related to the cleavage of Si–N bonds and simultaneous N_2 evaporation. The second step (–6%) is most probably caused by BN decomposition and seemingly not complete during the HT-TGA experiment. The absence of BN in a sample annealed for 5 h in an argon atmosphere was already demonstrated by IR spectroscopy.

The heat treatment of materials **3c**, **4c**, and **5c** leads to the formation of the expected thermodynamically stable phases BN, SiC, and C (and $B_{4+\delta}C$ in **4c**), which are high-temperature stable in multicomposite materials up to 2300 °C (1 bar N_2). The mass change during the HT-TGA is negligible, even though this experiment was performed in an argon atmosphere.

Summary

Si–B–C–N ceramics were synthesized by thermolysis of polymeric boron-containing silazanes or silylcarbodiimides with B/N atomic ratios ranging from 1:3 to 1:0.5. Ceramization of the highly cross-linked polymers at 1400 °C is accompanied by the loss of hydrogen and 31–45% of the carbon atoms. The compositions of the as-thermolyzed ceramics are located in or close to the phase fields BN + Si_3N_4 + C, BN + Si_3N_4 + SiC + C, BN + SiC + C, or BN + $B_{4+\delta}C$ + SiC + C and determine the high-temperature behavior. The SiC-poor (5 atom %) as-thermolyzed material **2c** is not stable at high temperatures. Si–N bonds are cleaved in the presence of free carbon between 1400 and 1600 °C, leading to an SiC/BNC/C multicomposite material. The compositions of ceramics containing SiC crystals in the as-thermolyzed state remain almost constant up to 2150 °C, even if Si_3N_4 is present; crystallization leads to the formation of the phases thermodynamically stable at 1400 °C and 1 bar N_2 .

Although phase evolution in Si_3N_4 -free materials seems to follow thermodynamic predictions, formation of the expected phases BN and C (and $B_{4+\delta}C$) is not clearly evidenced. To get more insight into the structural evolution of boron-containing phases at higher temperatures, investigations using transmission electron microscopy are in progress.

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft (DFG) for financial support. We are very grateful to Gerhard Kaiser (microanalytic investigations), Horst Kummer (high-temperature thermogravimetric measurements), and Martina Thomas (XRD studies).

CM021179A