Synthesis and High-Temperature Behavior of Si/B/C/N Precursor-Derived Ceramics without "Free Carbon"

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For the preparation of carbon-poor Si/B/C/N precursors, Si/C/N/H polymers with Si:C atomic ratios higher than or equal to 1 were synthesized by Wurtz-type coupling and subsequent ammonolysis of ClSiH(Me)NHSiH(Me)Cl and MeSiHCl$_2$ or H$_2$SiCl$_2$. They were reacted with a borane to obtain three different precursors which were transformed into Si/B/C/N ceramic materials by thermolysis at 1400 °C. Elemental analysis revealed that the crystallized samples should contain less than 6 atom % of "free carbon". The high-temperature behavior up to 2150 °C was investigated by thermogravimetric analysis and XRD of annealed samples. These results were compared with thermodynamic calculations using the CALPHAD approach.

1. Introduction

Solid state thermolysis is a versatile method for the preparation of precursor-derived ceramics.[1−3] Composition and microstructure of these materials can be controlled by tailoring the starting polymers and by variation of the experimental conditions. Ceramics containing the elements silicon, carbon, and nitrogen are easily prepared by thermolysis of polysilazanes or polysilylcarbodiimides (for recent reviews see refs 4 and 5). Heat treatment at about 1000 °C leads to the formation of amorphous inorganic materials with interesting thermomechanical properties[6,7] and oxidation behavior.[8,9] Crystallization at higher temperatures produces the thermodynamically stable phases Si$_3$N$_4$, SiC, C, or Si. The high-temperature stability of Si/C/N ceramics is limited by the presence of Si$_3$N$_4$.[10] According to calculation of phase diagrams (CALPHAD),[11] Si$_3$N$_4$ reacts with carbon at 1484 °C (1 atm N$_2$) with formation of SiC and nitrogen gas (reaction 1).[12]

$$Si_3N_4 + 3C \xrightarrow{1484\ °C} 3SiC + 2N_2\uparrow \qquad (1)$$

Furthermore, decomposition of silicon nitride into the elements is expected at about 1840 °C (reaction 2). In a stoichiometric Si$_3$N$_4$−SiC composite synthesized by Weinmann et al., however, crystalline Si$_3$N$_4$ could be detected by XRD even after annealing at 2000 °C for 3 h in a nitrogen atmosphere.[13]

$$Si_3N_4 \xrightarrow{1841\ °C} 3Si + 2N_2\uparrow \qquad (2)$$
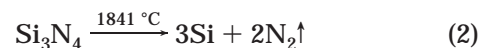
Within former studies it has been shown that many boron-containing Si/C/N ceramics are extraordinarily high-temperature stable (see, e.g., refs 14−16). The as-thermolyzed amorphous materials crystallized at about 1800 °C yielding composite materials[17] that consisted of silicon nitride and carbide nanocrystals with a size of about 50 nm. These nanocrystals were embedded into a boron-, carbon-, and nitrogen-containing turbostratic matrix. Because carbon is diluted within this phase by B and N atoms, its activity is reduced. Carbothermal reduction (reaction 1) is therefore shifted to higher temperatures compared to ternary solids. Another important effect is the encapsulation of Si$_3$N$_4$ nanocrystals by the BNC$_x$ matrix phase which provides closed nano-compartments.[18] Thus, N$_2$ created by carbothermal

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reduction (reaction 1) or by decomposition of Si_3N_4 into the elements (reaction 2) cannot escape leading to a pressure stabilization of the nitride. Obviously, the matrix phase in precursor-derived Si/B/C/N ceramics plays an important role. To gain more insight into the correlation of high-temperature stability and composition of the matrix, we synthesized ceramic materials without or with a small amount of "free carbon" and characterized their thermal behavior.

2. Experimental Section

2.1. General Comments. All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques. The chlorosilanes H_2SiCl_2 and $H_3CSiHCl_2$ were obtained from Aldrich (Germany), and $H_3CSiHCl_2$ was freshly distilled from Mg before use. $[(H_3C)_3Si]_2NH$ was purchased from Merck (Germany). 1,3-Dichloro-1,3-dimethyldisilazane was synthesized according to the literature[19] by reaction of $[(H_3C)_3Si]_2NH$ with excess $H_3CSiHCl_2$. Borane dimethyl sulfide (2 M solution in toluene) was obtained from Sigma-Aldrich (Germany). Diethyl ether and toluene were purified by distillation from CaH_2 and potassium, respectively.

Fourier transform infrared spectra were obtained with a Bruker IFS66 spectrometer as KBr pellets (solids) or as films in KBr cells (liquids). Raman spectra were recorded on a Bruker IFS 100 FT Raman spectrometer (NIR region) with a laser power of 200–500 mW at the Institut für Physikalische Chemie der Universität Stuttgart. Chemical analysis was performed using a combination of different analysis equipment (Elementar Vario EL, Eltra CS 800 C/S Determinator, and Leco TC-436 N/O Determinator), and by atom emission spectrometry (ISA JOBIN YVON JY70 Plus).

2.2. Precursor Synthesis. Results of chemical analysis of the polymers are given below in Table 1, Section 3.1.

2.2.1. PSSZ2. In a 1-L Schlenk flask equipped with a dropping funnel, a reflux condenser (both cooled to −5 °C), and a magnetic stirrer, a suspension of 24.6 g of sodium (1.07 mol) in 200 mL of toluene was heated to reflux. A mixture of 29.4 g of $H_3CSiHCl_2$ (0.26 mol) and 44.5 g of $(H_3CSiHCl)_2NH$ (0.26 mol) was added dropwise within 2 h whereby a gray precipitate formed in a dark blue solution. After refluxing for an additional 11 h, the mixture was cooled to room temperature and filtered through a pad of Celite. The precipitate was washed twice with 100 mL of diethyl ether. The solutions were combined and the solvents were partly distilled off to reduce the volume by 50%. A moderate stream of ammonia was introduced into this solution for 3 h at room temperature, whereby ammonium chloride was formed. The mixture was filtered, and the precipitate was washed with toluene. The solvents were removed from the combined solutions by distillation under reduced pressure. After drying the product at 70 °C (6×10^{-2} mbar), 28.3 g of **PSSZ2** was obtained as a yellow oil (yield 74.1%). IR (neat): 3401 w, 2958 m, 2893 w, 2133 s, br, 1408 w, 1255 s, 1170 w, 994 sh, 950 s, 896 vs, 762 m, 689 m cm⁻¹.

2.2.2. PSSZ9. In a 1-L Schlenk flask equipped with a dropping funnel, a reflux condenser (both cooled to −10 °C), and a magnetic stirrer, 450 mL of toluene was added to 17.6 g of $K_{1.9}Na$ alloy (13.5 g (345 mmol) of K and 4.1 g (178 mmol) of Na) and cooled to −15 °C. A mixture of 15.0 g of $(H_3CSiHCl)_2NH$ (86 mmol) and 11.4 g of H_2SiCl_2 (172 mmol) was added dropwise within 45 min. The mixture was stirred for 5 h at −10 to −15 °C and for 30 h at room temperature. The precipitate was removed by filtration. Ammonia was introduced into the solution at 0–5 °C for 0.5 h. After separation of ammonium chloride by filtration, the solvents were distilled off under reduced pressure. Drying the product at 70 °C (5×10^{-2} mbar) yielded 11.3 g of bright yellow oily **PSSZ9** (82%).

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IR (neat): 3380 w, 2958 w, 2900 w, 2858 vw, 2140 s, br, 1407 w, 1255 s, 1177 s, 994 sh, 938 s, 881 vs, 758 m cm⁻¹.

2.2.3. PSSZ2-2B, PSSZ2-3B, PSSZ9B. To a solution of **PSSZ** in toluene, a 2 M solution of $H_3B\cdot SMe_2$ was added dropwise at 0–5 °C within 10–20 min. The mixture was subsequently stirred for 1.5 h at this temperature, then allowed to warm to room temperature overnight. After refluxing for 6 h, the solvent was removed by distillation under reduced pressure. The residual dark-brown solid was dried in a vacuum (6×10^{-2} mbar) at 50 °C.

2.2.3.1. **PSSZ2-2B:** 5.0 g of **PSSZ2** in 20 mL of toluene, 20.0 mL of 2 M $H_3B\cdot SMe_2$ (40 mmol), yield 5.3 g (97%). IR (KBr): 3433 vw, 2958 m, 2891 vw, 2522 m, br, 2140 s, br, 1405 sh, 1376 m, 1317 m, 1257 s, 1157 m, 994 s, 950 s, 900 vs, 762 m, 689 w cm⁻¹.

2.2.3.2. **PSSZ2–3B**: 12.2 g of **PSSZ2** in 50 mL of toluene, 65.6 mL of 2 M $H_3B\cdot SMe_2$ (131 mmol), yield 12.1 g (88%). IR (KBr): 3425 vw, 2958 m, 2926 w, 2893 w, 2854 vw, 2516 m, br, 2141 s, br, 1405 sh, 1377 m, 1310 m, 1257 s, 1156 m, 994 s, 950 s, 901 vs, 761 m, 689 w cm⁻¹.

2.2.3.3. **PSSZ9B**: 10.0 g of **PSSZ9** in 90 mL of toluene, 48.3 mL of 2 M $H_3B\cdot SMe_2$ (97 mmol), yield 9.8 g (88%). IR (KBr): 3423 w, 2960 m, 2925 w, 2901 w, 2854 vw, 2477 m, br, 2152 s, br, 1400 sh, 1377 m, 1310 m, 1257 s, 1154 m, 995 sh, 951 s, 897 vs, 843 vs, 754 m cm⁻¹.

2.3. Ceramization and Heat Treatment. The polymer-to-ceramic transformation was investigated by thermogravimetric analysis (25–1400 °C; heating rate, 5 °C/min) in a flowing argon atmosphere with Netzsch STA 409 equipment in alumina crucibles. Bulk samples were thermolyzed in Al_2O_3 Schlenk tubes in a flowing argon atmosphere (heating rate, 25–1400 °C, 1 °C/min followed by a dwell time of 2 h).

High-temperature thermogravimetric analysis of the as-obtained ceramic materials was performed in a nitrogen atmosphere using BN crucibles (25–2150 °C; heating rates $T < 1400$ °C, 10 °C/min; $T > 1400$ °C, 5 °C/min) with Netzsch STA 501 equipment.

The crystallization was performed in graphite furnaces using BN crucibles (heating rates $T < 1400$ °C, 10 °C/min; $T > 1400$ °C, 2 °C/min; dwell time, 3 h) in a nitrogen atmosphere. The annealed samples were investigated by X-ray diffraction with a Siemens D5000/Kristalloflex (Cu Kα_1 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.

3. Results and Discussion

3.1. Precursor Synthesis. According to the procedure described by Mocaer et al.,[19] boron-free polymers containing the elements silicon, carbon, nitrogen, and hydrogen were prepared by reaction of 1,3-dichloro-1,3-dimethyldisilazane and a chlorosilane with an alkali metal. A suspension of molten sodium in boiling toluene is sufficiently reactive to produce this Wurtz-type coupling, but, unfortunately, high temperatures are required. Therefore, volatile silanes in all probability are not suitable for this procedure.

Starting from dichlorodimethylsilane (boiling point 70 °C) and 1,3-dichloro-1,3-dimethyldisilazane, the polymers synthesized by Mocaer et al.[19] were composed of $[-SiMe_2-]$ and $[-MeSiH-NH-HSiMe-]$ building blocks with an atomic ratio Si:C smaller than 1. Even though this ratio increased during thermolysis, the resulting ceramic materials contained a small amount of "free carbon" which is supposed to deteriorate the high-temperature stability (see below).

To reduce the amount of carbon within the polymer, we used dichloromethylsilane Cl_2SiHMe or dichlorosilane Cl_2SiH_2 instead of dichlorodimethylsilane (reaction 3). Because of the problems mentioned above (the boiling

Table 1. Composition of Polymers (wt %) (Theoretical Values in Parentheses)

compound	Si	B	C	N	H	O	formula[a]
PSSZ2	54.0		24.3	15.0	7.4	n.d.	$Si_3C_{3.2}N_{1.7}H_{11.5}$
	(57.2)		(24.4)	(9.5)	(8.9)	(0.0)	$(Si_3C_3NH_{13})$
PSSZ9	52.6		15.1	25.1	6.8	1.2	$Si_3C_{2.0}N_{2.9}H_{10.8}$
	(68.7)		(14.7)	(8.6)	(8.0)	(0.0)	$(Si_4C_2NH_{11})$
PSSZ2−2B	47.5	7.5	22.5	12.7	7.2	0.4	$Si_3B_{1.2}C_{3.3}N_{1.6}H_{12.7}$
	(49.1)	(7.9)	(22.1)	(13.5)	(7.5)	(0.0)	$(Si_3B_{1.3}C_{3.2}N_{1.7}H_{12.7})$
PSSZ2−3B	46.5	9.6	21.8	13.4	6.8	1.6	$Si_3B_{1.6}C_{3.3}N_{1.7}H_{12.2}$
	(47.5)	(10.4)	(21.4)	(13.2)	(7.5)	(0.0)	$(Si_3B_{1.7}C_{3.2}N_{1.7}H_{13.2})$
PSSZ9B	47.7	8.4	14.1	21.7	5.5	2.3	$Si_3B_{1.4}C_{2.1}N_{2.7}H_{9.6}$
	(47.4)	(9.4)	(13.6)	(22.6)	(7.0)	(0.0)	$(Si_3B_{1.5}C_{2.0}N_{2.9}H_{12.3})$

[a] O content is neglected.

points of Cl_2SiHMe and Cl_2SiH_2 are at 42 and 8 °C, respectively), efficient cooling of the reflux condenser was needed to prevent evaporation of the silanes during synthesis. Furthermore, the reduction of Cl_2SiH_2 and $(MeSiHCl)_2NH$ was performed at low temperature (−15 °C) with liquid K/Na alloy instead of molten Na. In this case, however, a large excess of the volatile silane was used. Empirically we found that 2 equiv were necessary to guarantee a stoichiometric 1:1 reaction.


$$R = H, CH_3$$

PSSZ2: R=CH₃
PSSZ9: R=H
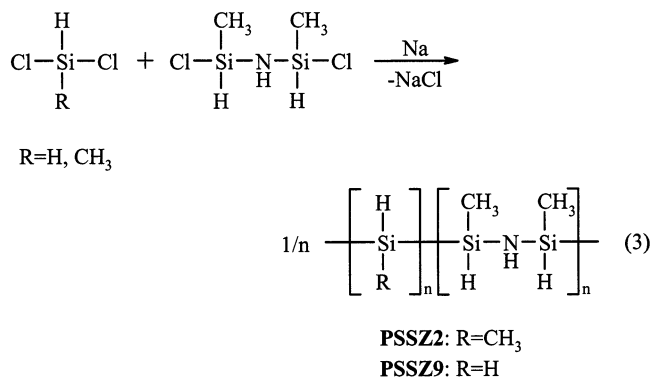
The scheme depicted in reaction 3 is idealized. Despite long reaction times, silane coupling is not quantitative under these conditions and Cl atoms remain attached to Si atoms. As proposed by Mocaer et al.,[19] the raw products were subsequently treated with ammonia to exchange Si−Cl groups for Si−(NH)$_{0.5}$ units. By this procedure, however, the nitrogen content of the polymers increased.

PSSZ2 synthesized from Cl_2SiHMe and $(MeSiHCl)_2NH$ should contain [−SiHMe−] and [−MeSiH−NH−HSi−Me−] building blocks, whereas **PSSZ9** should be composed of [−SiH$_2$−] and [−MeSiH−NH−HSiMe−] units. IR spectra of **PSSZ2** and **PSSZ9** were very similar. N−H stretching and Si−N−H deformation vibrations were detected around 3380−3400 cm^{-1} and 1170−1177 cm^{-1}, respectively. These absorptions were significantly stronger in **PSSZ9** than in **PSSZ2** due to the higher N concentration of the former material (see below). Methyl groups revealed their presence by vibration bands at 2958−2858 (ν C−H), 1255 cm^{-1} (ρ SiCH$_3$), and 940−950 cm^{-1} (δ CH). Strong absorptions at 2133 and 900 (**PSSZ2**) or 2140 cm^{-1} and 897/843 cm^{-1} (**PSSZ9**) can be assigned to the Si−H stretching and deformation vibration, respectively. NMR spectra of **PSSZ2** and **PSSZ9** are in accordance with these structural elements. They will be discussed elsewhere along with spectroscopic results on the ceramization process.

Elemental composition of these Si−C−N−H polymers is given in Table 1. In both cases the Si concentration

is lower than the theoretical value. This is most probably caused by evaporation of volatile silanes as discussed above. The composition of **PSSZ9** ($Si_3C_{2.0}N_{2.9}H_{10.8}$) determined by chemical analysis shows that only one equiv of Cl_2SiH_2 was incorporated into the polymer. Furthermore, the nitrogen content is much higher than calculated. The N:Si atomic ratio which was supposed to be 1:3 (according to reaction 3) is increased to 1.7:3 in **PSSZ2** and to almost 3:3 in **PSSZ9** showing the inefficiency of alkali metal coupling of silanes which is extremely pronounced at low temperature using K/Na alloy (**PSSZ9**). Consequently, the actual structure of **PSSZ2** is better described by the formula [−MeSiH−NH−HSiMe−(NH−)$_x$]$_n$[−SiHMe−(NH−)$_y$]$_n$ ($x + y = 0.7$), whereas **PSSZ9** is predominantly composed of [−MeSiH−NH−]$_n$[−SiH$_2$−NH]$_n$ building blocks.

By incorporation of boron atoms into the polymers, the concentration of free carbon within the ceramics should be reduced. Due to preferred formation of B−N bonds,[17] the amount of nitrogen available for the generation of Si_3N_4 decreases. Consequently, the SiC concentration increases and less carbon remains "free". We modified the Si−C−N−H polymers **PSSZ2** and **PSSZ9** by reaction with $H_3B\cdot SMe_2$ to produce Si−B−C−N ceramics without free carbon upon thermolysis. The reaction took place without catalyst via dehydrocoupling of the silazane N−H units and B−H groups as shown below schematically (reaction 4). If the boron content is lower than the nitrogen content, the borane having three B−H groups provides a means to crosslink disilazane chains by reaction with residual N−H centers.

$$R = H, CH_3$$
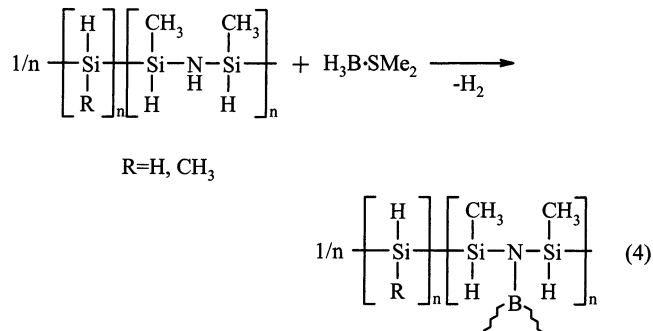
To calculate the amount of borane to be added, **PSSZ2** was reacted with $H_3B\cdot SMe_2$ in a 3:4 stoichiometric ratio to obtain the polymer **PSSZ2−2B** ($Si_3B_{1.2}C_{3.3}N_{1.6}H_{12.7}$) which was subsequently thermolyzed. The composition of this ceramic (see Table 2) was determined analytically. On the assumption that the change of the Si:C:N ratio during thermolysis is not significantly affected by

Table 2. Composition of Ceramic Materials (wt %; atom % in Parentheses)

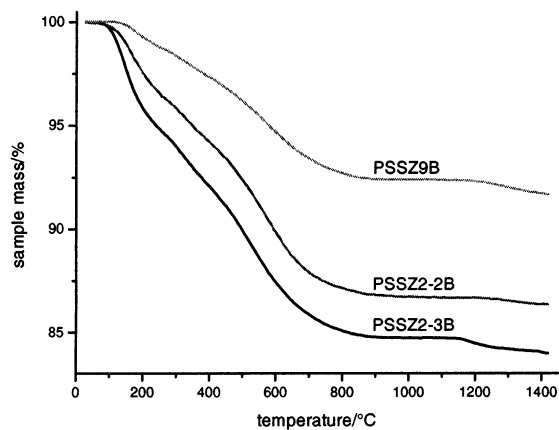| compound	Si	B	C	N	H	O	ceramic formula[a]	polymer formula
PSSZ2−2BC	51.7 (33)	8.2 (14)	22.3 (33)	16.2 (21)	<0.1	0.8	$SiB_{0.4}C_{1.0}N_{0.6}$	$SiB_{0.4}C_{1.1}N_{0.5}H_{4.2}$
PSSZ2−3BC	49.4 (32)	10.7 (18)	19.1 (29)	17.2 (22)	0.2	1.6	$SiB_{0.6}C_{0.9}N_{0.7}$	$SiB_{0.5}C_{1.1}N_{0.6}H_{4.1}$
PSSZ9BC	50.2 (32)	10.4 (17)	14.1 (21)	24.4 (31)	<0.1	1.0	$SiB_{0.5}C_{0.7}N_{1.0}$	$SiB_{0.5}C_{0.7}N_{0.9}H_{3.2}$

[a] H, O content neglected.

Figure 1. Thermogravimetric analysis of polymers **PSSZ2−2B**, **PSSZ2−3B**, and **PSSZ9B** (20−1450 °C; heating rate, 5 °C/min; Ar atmosphere).

the presence of boron, we adjusted the stoichiometric parameters in reaction 4 to obtain the Si/B/C/N precursor **PSSZ2−3B** ($Si_3B_{1.6}C_{3.3}N_{1.7}H_{12.2}$) which could be transformed into a ceramic material containing no "free carbon" (see below). In a similar way, the reaction of **PSSZ9** with borane was calculated to produce the Si/B/C/N precursor **PSSZ9B**.

Compared to the boron-free starting polymers **PSSZ2** and **PSSZ9**, the position of the absorption bands in the IR spectra changed slightly. As expected, the intensity of the N−H vibration bands decreased after dehydrocoupling. Very broad structured absorptions at about 2520 (**PSSZ2−2B** and **PSSZ2−3B**) or 2480 cm^{-1} (**PSSZ9**) indicated the presence of B−H units. The formation of B−N bonds was evidenced by vibration bands at 1376 cm^{-1}.

Results of chemical analysis of the polymers are given in Table 1. Theoretical values were calculated from the compositions of boron-free materials **PSSZ2** and **PSSZ9** which were found analytically. Furthermore, it was assumed that each borane unit reacts with one N−H group (according to reaction 4) releasing one equivalent of H_2.

The Si:C:N atomic ratios of polymers **PSSZ2−2B** (3: 3.3:1.6) and **PSSZ2−3B** (3:3.3:1.7) were very similar, whereas compound **PSSZ9B** contained less carbon and more nitrogen atoms (3:2.1:2.7). The boron content increased from 7.5 wt % in **PSSZ2−2B** to 8.4 wt % in **PSSZ9B** and 9.6 wt % in **PSSZ2−3B**.

3.2. Ceramization of the Polymers. The boron-containing polymers were converted into ceramic materials by thermolysis at 1400 °C in an argon atmosphere. The mass loss during this transformation was monitored by thermogravimetric analysis (Figure 1). Decomposition of the polymers is characterized by three steps. The first mass loss was observed between about 100 °C (**PSSZ2−2B** and **PSSZ2−3B**) or 130 °C

(**PSSZ9B**) and 220 °C. This mass reduction is more pronounced during thermolysis of **PSSZ2−3B** (5%) compared to **PSSZ2−2B** (3%), whereas it was negligible for **PSSZ9B** (1%). It was probably caused by evaporation of small silicon-containing molecules as silanes or silazanes which were not sufficiently linked to the polymer backbone. As suggested above (see Section 3.1) as-obtained polymers with a high B:N ratio should be less highly cross-linked than those with a small B:N ratio. With this value being close to 1 for **PSSZ2−3B**, N−BH$_2$ units will form during synthesis (reaction 4) and the molecular mass of the precursors will not be significantly increased by addition of the borane. Decrease of the B:N ratio to 0.75 in **PSSZ2−2B** and 0.5 in **PSSZ9B** supports cross-linking of the silazane chains by formation of N−BH−N or BN$_3$ centers. Furthermore, residual N−H groups in **PSSZ9B** and **PSSZ2−2B** will most probably react with Si−H units by dehydrocoupling.

The most important mass loss was detected between 220 and 900 °C. In this temperature range, cleavage of organic groups and of hydrogen was observed by Mocaer et al. in similar precursors.[19] Because **PSSZ2−2B** and **PSSZ2−3B** have the same Si/C/N polymer backbone structure, decomposition of these two materials was very similar, leading to an evaporation of 10% of the original mass whereas the loss observed for **PSSZ9B** which contains fewer methyl groups is slightly smaller (7%).

At temperatures higher than 900 °C, the composition of the materials did not change significantly. The small mass losses (<1%) starting at 1150 (**PSSZ2−3B** and **PSSZ9B**) or 1220 °C (**PSSZ2−2B**) are most probably due to evaporation of residual hydrogen gas.[19]

The composition of the materials obtained after thermolysis (denoted by the polymer name followed by **C**) is given in Table 2. The ceramics and the corresponding polymers have very similar Si/B/C/N ratios. This indicates that, apart from H$_2$, the gaseous thermolysis products have the same overall composition as the polymers. According to TGA measurements, however, the amount of Si/B/C/N containing molecules lost during the heat treatment is low.

3.3. High-Temperature Behavior. Starting from the overall formulas of the ceramic materials obtained after thermolysis at 1400 °C (Table 2), the amount of thermodynamically stable phases which should be present in a completely crystallized sample can be calculated by means of the calculation of phase diagrams approach (CALPHAD).[11] Results are given in Table 3. According to these calculations, the formation of composite materials containing BN, Si$_3$N$_4$, and SiC (and additionally 6 atom % of "free carbon" in **PSSZ2−2BC**) was expected.
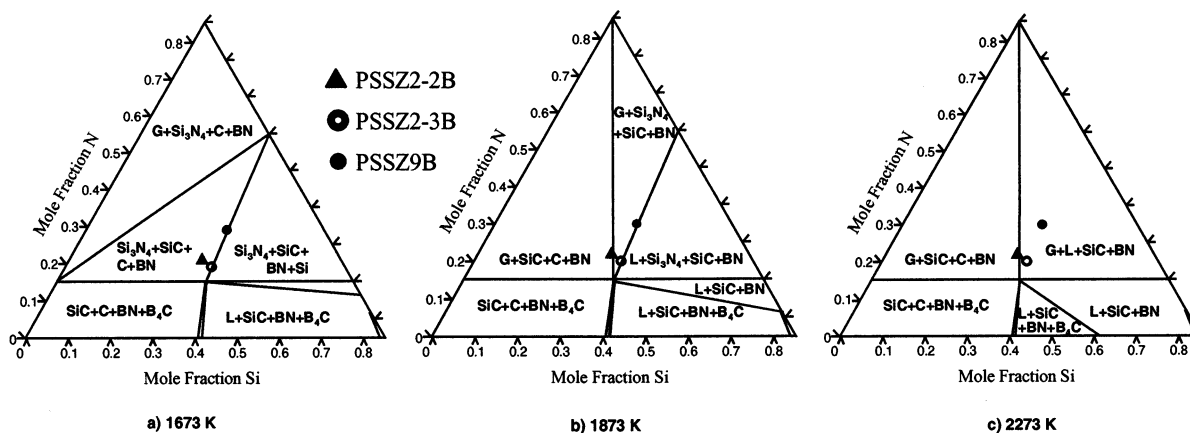
Figure 2. Isothermal sections of the Si/B/C/N phase diagram at 15 atom % boron at (a) 1400 °C, (b) 1600 °C, and (c) 2000 °C, 1 atm N_2.[20] The compositions of as-thermolyzed materials **PSSZ2−2BC**, **PSSZ2−3BC**, and **PSSZ9BC** are indicated.

Table 3. Calculated Relative Phase Fractions (atom %, O content is neglected) of Ceramic Materials and Calculated Mass Changes Due to Si_3N_4 Decomposition

compound	BN	Si_3N_4	SiC	C	Δm_1 (1484 °C)	Δm_2 (1841 °C)
PSSZ2−2BC	27	12	55	6	−5.5%	0%
PSSZ2−3BC	36	7	57	0	0%	−3.2%
PSSZ9BC	34	24	42	0	0%	−11.1%

To illustrate these results and to predict the high-temperature behavior by thermodynamic means, phase equilibria for different temperatures were considered.[20,21] In Figure 2 the compositions of as-obtained materials are inserted into the diagrams which represent isothermal sections of the Si/B/C/N system at a constant boron concentration of 15 atom % at 1400, 1600, and 2000 °C, respectively, in a nitrogen atmosphere (1 atm). At 1400 °C, the compositions of **PSSZ2−3BC** and **PSSZ9BC** lie within the three-phase equilibrium field Si_3N_4 + SiC + BN, whereas that of compound **PSSZ2−2BC** is located within the four-phase field Si_3N_4 + SiC + C + BN (Figure 2a). The latter is not stable at temperatures higher than 1484 °C due to carbothermal reduction of silicon nitride in the presence of carbon (reaction 1). This material should decompose, releasing nitrogen to form a BN/SiC/C composite at 1600 °C (Figure 2b). A mass loss Δm_1 of 5.5% is expected for this reaction. The compositions of **PSSZ2−3BC** and **PSSZ9BC** are supposed to remain unchanged at this temperature. Thermodynamic calculations furthermore predict decomposition of Si_3N_4 into the elements at 1841 °C (reaction 2). Evaporation of N_2 should lead to a mass change Δm_2 of −3.2% in **PSSZ2−3BC** and of −11.1% in **PSSZ9BC**, whereas up to 2000 °C (Figure 2c), mass stability is expected for the BN/SiC/C composite derived from **PSSZ2−2BC**.

On the basis of these calculations and of former TEM results on carbon-rich Si/B/C/N ceramics,[17,22] crystallized samples should be composed of SiC and Si_3N_4 nanocrystals embedded in a matrix. This matrix phase should consist of BN in materials **PSSZ2−3BC** and **PSSZ9BC**, whereas in **PSSZ2−2BC** "free carbon"
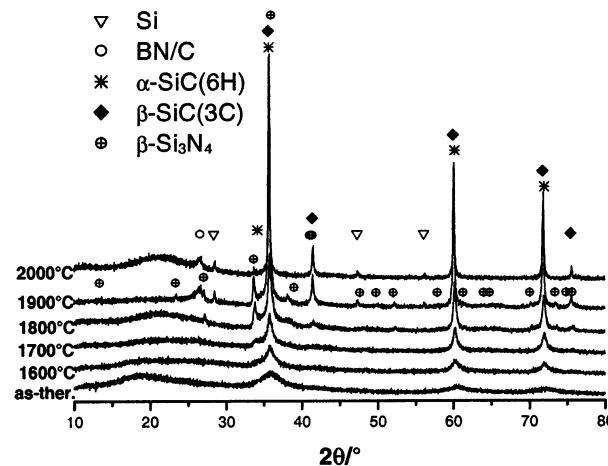
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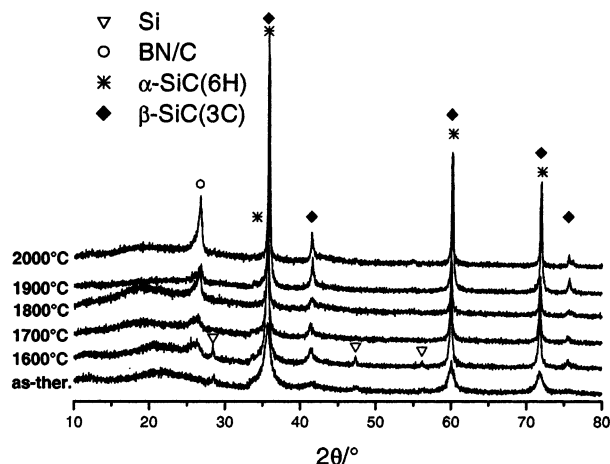

Figure 3. XRD of as-thermolyzed and annealed **PSSZ2−2BC** (1600−2000 °C, 100 °C steps; dwell time, 3 h; N_2 atmosphere).

should be incorporated into the matrix to form a turbostratic BNC_x phase.

3.3.1. X-ray Diffraction (XRD). To characterize the high-temperature behavior of the ceramic materials, as-thermolyzed samples were annealed at 1600−2000 °C (100 °C steps) for 3 h in a nitrogen atmosphere and subsequently analyzed by XRD.

After thermolysis, **PSSZ2−2BC** was predominantly amorphous (Figure 3). Very broad reflections at about 36, 60, and 72° were observed which can be attributed to nanocrystalline SiC. These signals sharpened increasingly after annealing at higher temperatures. Reflections of a second crystalline phase were detected at 1800 °C. They indicate the presence of β-Si_3N_4. The intensity of these signals increased after heat treatment at 1900 °C. Besides, the presence of elemental silicon could be evidenced at this temperature. According to thermodynamic calculations (reaction 2, see above), Si_3N_4 should decompose completely at about 1840 °C to form silicon and nitrogen gas. This reaction seems to be retarded in material **PSSZ2−2BC**. A broad reflection at about 26° can be assigned to a BN or C containing phase (BNC_x) which is most probably turbostratically ordered. BN and C were already detected in the as-thermolyzed material by IR (1380 cm^{-1} s, ν B−N) and Raman spectroscopy (1313 vb (D band) and 1600 cm^{-1} sh (G band)), respectively. At 2000 °C finally, Si_3N_4 reflections were absent and the material was composed of BNC_x, SiC, and Si.

Figure 4. XRD of as-thermolyzed and annealed **PSSZ2−3BC** (1600−2000 °C, 100 °C steps; dwell time, 3 h; N₂ atmosphere).

Figure 5. XRD of as-thermolyzed and annealed **PSSZ9BC** (1600−2000 °C, 100 °C steps; dwell time, 3 h; N₂ atmosphere).

Figure 6. HTTGA of as-thermolyzed materials **PSSZ2−2BC**, **PSSZ2−3BC**, and **PSSZ9BC** (1300−2150 °C, N₂ atmosphere, heating rate, $T < 1400$ °C, 10 °C/min; $T > 1400$ °C, 5 °C/min).

In as-thermolyzed **PSSZ2−3BC** (Figure 4), SiC reflections were significantly sharper than those for **PSSZ2−2BC**, which is probably due to the formation of larger crystals. Furthermore, signals revealing the presence of "free silicon" were detected. According to elemental analysis and thermodynamic calculations (see above), the material should be composed of BN, Si_3N_4, and SiC only. Obviously, as-thermolyzed **PSSZ2−3BC** is far from equilibrium. The formation of silicon during thermolysis may be a consequence of the polymer structure. The precursor **PSSZ2−2B** (and **PSSZ2−3B**) contained Si−Si bonds which were formed during the Wurtz-type coupling reaction (see reaction 3) and subsequent cross-linking. During thermolysis, these bonds may have survived if the reaction with carbon to form SiC was kinetically hindered. In comparison with **PSSZ2−3B**, the formation of SiC in **PSSZ2−2B** is preferred because of the higher carbon concentration. After annealing at 1600 °C, the intensity of Si and SiC signals increased. Additionally, a very broad reflection was observed at about 26°. The position corresponds to the main reflection peak of hexagonal BN or C. The microstructure obtained after the heat treatment at 1700 °C is composed of crystalline SiC and BN(+C). Silicon reflections were not detected. At this temperature, silicon is very reactive and will most probably form Si_3N_4 in a nitrogen gas atmosphere (see HTTGA below). The absence of Si_3N_4 reflections in the diffraction diagram indicates that the amount of crystalline Si_3N_4 is very small. At 1800, 1900, and 2000 °C, the intensity and sharpness of the reflections increased, signaling grain growth of the crystallites and an increasing order of the turbostratic phase. The final microstructure at 2000 °C mainly contained β-SiC and well-ordered BN. Reflections of Si_3N_4 were not observed during these heat-treatment experiments.

PSSZ9BC was predominantly amorphous after thermolysis (Figure 5). Broad reflections at 36, 60, and 72° indicated the presence of SiC nanocrystals. Elemental silicon was not detected in this material. In contrast to **PSSZ2**, the starting polymer **PSSZ9** used for the synthesis of **PSSZ9B** was mainly composed of [−MeSiH−NH−]$_n$[−SiH₂−NH]$_n$ building blocks. Si−Si bonds were absent in this precursor and their formation during thermolysis by dehydrogenative coupling of Si−H + H−Si units is improbable (dehydrocoupling of Si−H +
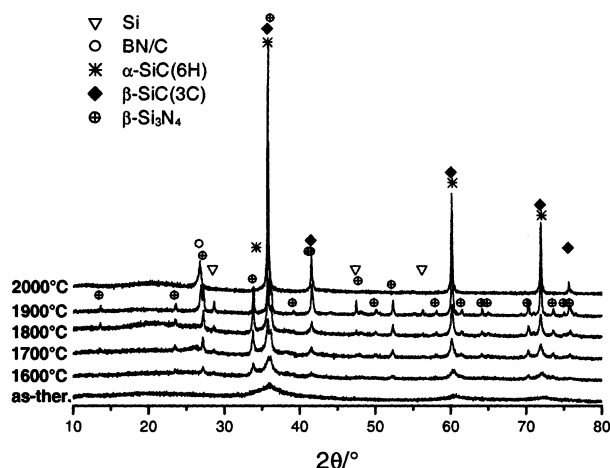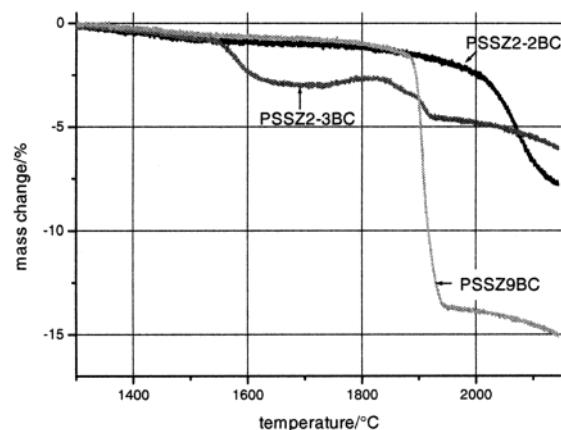
H−N centers is preferred in **PSSZ9B** which has the highest NH content in this series). After annealing at 1600 °C, the intensity of SiC signals was slightly increased. Besides, very small reflections of β-Si_3N_4 and Si were observed. At 1700 °C, an additional very broad signal at 26° indicated the presence of BN. The intensity of all reflections increased gradually after annealing at 1800 and 1900 °C. Crystalline phases detected in the 2000 °C sample were SiC and BN. Obviously, Si_3N_4 decomposed at this temperature according to thermodynamic predictions (reaction 2).

3.3.2. High-Temperature Thermogravimetric Analysis (HTTGA). The high-temperature behavior of as-obtained materials **PSSZ2−2BC**, **PSSZ2−3BC**, and **PSSZ9BC** was additionally investigated by thermogravimetric analysis up to 2150 °C in a nitrogen atmosphere. Results are illustrated in Figure 6. The mass change of **PSSZ2−2BC**, which contains 6 atom % of "free carbon", was continuous but very small up to 2000 °C (ca. 2.5%). In contrast to thermodynamic calculations, mass losses due to carbothermal reduction at 1484 °C (reaction 1, Table 3) were not detected. At higher temperatures decomposition proceeded faster. During the experiment a total mass loss of 7.8% was observed. The actual mass change of −5.3% between 2000 and 2150 °C can be attributed to complete Si_3N_4 decomposition, as it corresponds to the amount of nitrogen present in Si_3N_4 (see Table 3). These results

are in accordance with XRD analysis (see above) showing the presence of crystalline Si_3N_4 after annealing at 1900 °C for 3 h. The HTTGA of **PSSZ2−3BC** reveals a different behavior. A first mass loss was detected between 1550 and 1640 °C, leading to a mass reduction of about 2%. According to XRD measurements and elemental analysis (see above), as-thermolyzed **PSSZ2−3BC** contains "free silicon" and consequently "free carbon". The latter is supposed to react with silicon nitride at about 1500 °C (reaction 1) causing a weight loss by evaporation of nitrogen. The mass gain observed in the TGA diagram between 1740 and 1810 °C is most probably a consequence of "free silicon" reacting with the nitrogen gas atmosphere to form Si_3N_4. This was not detected when the experiment was performed in an argon atmosphere (not shown here). The total mass loss of **PSSZ2−3BC** between 1550 and 1920 °C amounted to 3.7% and was close to the mass of nitrogen present in Si_3N_4 (3.2%). The absence of Si_3N_4 reflections in the XRD diagrams of **PSSZ2−3BC** is most probably a consequence of the small amount of Si_3N_4 present within the sample at 1700 and 1800 °C. At higher temperatures decomposition proceeded very slowly. The high-temperature behavior of **PSSZ9B** followed thermodynamic predictions in the main. The sample mass remained almost constant up to 1880 °C (−1.5%). In a single reaction step between 1880 and 1950 °C, decomposition occurred, leading to a mass reduction of 12.2%, whereas the calculated value Δm_2 amounts to 11.1%. Evaporation of gas species at higher temperatures was negligible.

3.3.3. Conclusions. HTTGA and XRD results suggest that "free carbon" may play an important role in stabilizing precursor-derived Si/B/C/N ceramics against thermal decomposition. Whereas phase composition and thermal behavior of materials **PSSZ2−3BC** and **PSSZ9BC**, which did not contain significant amounts of "free carbon", followed thermodynamic calculations in the main, the high-temperature stability of **PSSZ2−2BC** (6 atom % of "free carbon") was clearly improved compared to thermodynamic predictions. In this material, the reaction of C with Si_3N_4 at 1484 °C (reaction 1) was not observed and decomposition of Si_3N_4 into the elements (1841 °C, reaction 2) was significantly retarded. These effects are more pronounced in short-term experiments such as TGA, indicating a kinetic stabilization.

The presence of "free carbon" in **PSSZ2−2BC** was demonstrated by Raman spectroscopy but the vibration bands were very broad and weak. The distribution of C within the sample is more difficult to establish by spectroscopic or microscopic means. C is most probably incorporated into the BN phase since the shape and position of the reflection peak correspond to those of carbon-rich Si/B/C/N ceramics which were analyzed by transmission electron microscopy.[17,22] The activity of carbon is reduced by this dilution, and reaction with Si_3N_4 is shifted to higher temperatures. Furthermore, the BNC_x matrix phase provides nanocompartments for the encapsulation of Si_3N_4, the decomposition of which is retarded in this way. The results obtained in our study suggest that these nanocompartments are more stable in a BNC_x than in a BN matrix phase. A comparison of the XRD diagrams of **PSSZ2−2BC**,

PSSZ2−3BC, and **PSSZ9BC** shows that crystallization of the BN phase in **PSSZ2−3BC** and **PSSZ9BC** started at about 1600−1700 °C. At 2000 °C, sharp and intense reflections were observed. In contrast to this, a very broad BN(+C) signal in **PSSZ2−2BC** was detected only after annealing at 1900 °C. These findings are in accordance with former studies on the crystallization behavior of turbostratic B/C/N and BN. Whereas transformation of BN into the thermodynamically stable crystalline phase was nearly complete at 1700−1800 °C,[23] B/C/N materials remained amorphous after annealing at 1800 °C.[24,25] Crystallization of the matrix phase in the Si/B/C/N ceramics described here most probably leads to destruction of the nanocompartments followed by decomposition of Si_3N_4. Therefore, the role of "free carbon" in these materials consists of stabilizing the amorphous (or turbostratic) matrix phase against crystallization in order to guarantee a fine microstructure.

IV. Summary

Within this study, $ClSiH(Me)NHSiH(Me)Cl$ was reacted with $MeSiHCl_2$ or H_2SiCl_2 in the presence of Na or K/Na alloy to prepare two Si/C/N/H polymers. This Wurtz-type coupling proved to be not very efficient, especially when K/Na was used at low temperatures. Residual chlorine atoms were removed by an ammonolysis reaction. The Si/C/N/H polymers were subsequently treated with different amounts of borane dimethyl sulfide. The three resulting Si/B/C/N precursors were transformed into predominantly amorphous ceramic materials in 84−92% yield by thermolysis at 1400 °C. The compositions of two of them were located within the phase field $BN + Si_3N_4 + SiC$, whereas the third additionally contained 6 atom % of "free carbon". The latter material was high-temperature mass stable in short-term experiments up to 2000 °C in a nitrogen atmosphere. Decomposition of Si_3N_4 started at about 1800−1900 °C but proceeded very slowly. The thermal stability of ceramics without "free carbon" was limited by Si_3N_4 decomposition which was observed as a fast mass loss at 1900 °C. According to XRD and HTTGA, "free carbon" most probably retards crystallization of the BN-based matrix phase. In this way, a distinct microstructure is formed in which Si_3N_4 degradation is efficiently slowed. To support these assumptions, TEM investigations are in progress dealing with the elemental distribution and crystallization of the matrix phase.

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