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Correlation of boron content and high temperature stability in Si–B–C–N ceramics II

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Abstract

This study treats the preparation of polyborosilazanes which are obtained by hydroboration of oligovinylsilazane [–(H_2C=CH)SiHNH–]$_n$ with different amounts of $H_3B{\cdot}SMe_2$. Pyrolysis of these precursors yields amorphous ceramic materials, which only differ in their relative boron content whereas their Si/C/N ratio is very similar. High temperature thermogravimetric analysis reveals that with increasing boron content the material's thermal degradation is shifted toward higher temperatures. Furthermore, the observed mass loss due to nitrogen evaporation during the material's decomposition is noticeably smaller in boron-rich materials than thermodynamically calculated. X-ray diffraction (XRD) experiments support the presence of crystalline silicon nitride in heat treated samples with a minimum boron content of 5 at.%. The decomposition temperature of this phase strongly depends on the amount of boron and can exceed 2000°C. However, high temperature stable materials are not only characterized by a definite B/N ratio, but also by the ability to develop appropriate microstructures. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The synthesis of ceramic materials containing the elements silicon, boron, carbon and nitrogen via pyrolysis of element-organic polymers[1–6] is a field of current investigations. The possibilities to vary the structure and compositions of the polymers allow a tailoring of desired properties of the precursors and the ceramic materials. In contrast to materials derived from Si–C–N precursors, the incorporation of boron can lead to ceramics with an outstanding high temperature stability.[7–10] The reasons for this remarkable characteristic are not yet understood in detail. In several recent publications it was shown that boron retards the crystallization during heat treatment experiments.[9–15] Furthermore, boron favours the development of a turbostratic BN(C) matrix phase that seems to be suitable to thermally stabilize silicon nitride: high resolution transmission electron microscopy revealed, that nano-sized crystals of SiC and Si_3N_4 are embedded in a carbon-rich B–C–N matrix consisting of turbostratic layers.[16] This phase is supposed to be an effective diffusion barrier that retards the decomposition of silicon nitride because (1) the activity of carbon integrated in these B–C–N layers is reduced in comparison with "free carbon"; (2) nitrogen gas formed by decomposition reactions cannot escape and leads to an internal pressure stabilization.[17,18] At standard conditions (1 atm N_2), Si_3N_4 decomposes at 1840°C [see Eq. (1)] and it reacts in the presence of carbon at 1481°C according to reaction (2).[19]

$$Si_3N_4 \rightarrow 3Si + 2N_2\uparrow \qquad (1)$$

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

Comparative studies of the high temperature characteristics of Si–B–C–N ceramics indicate that the incorporation of boron does not lead perforce to mass stability during heat treatment experiments.[20–22] The molecular structure of the polymeric precursors and the atomic ratios of the single elements determine the thermal properties of these materials.

From the structural point of view, a crucial subject is a homogenous distribution of the elements in the precursor. Initial de-mixing in the polymeric state by e.g.

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formation of borazine units always results in ceramics with a relative poor high temperature stability.[1,5,6] The influence of the Si/B/C/N ratio on the materials high temperature properties is — even though investigated thoroughly — still not known in detail, but it is supposed that the polymeric precursors should not exceed a certain nitrogen content.[17] In contrast, little is known about the influence of different amounts of boron on high temperature properties.

Therefore, in a first attempt, a systematic study was undertaken to synthesize precursors with the same basic structure and Si/C/N ratio, which only differ in their relative boron content.[23] For this, polymethylvinylsilazane, $[-(H_2C{=}CH)Si(CH_3)NH-]_n$, was reacted with different amounts of borane dimethylsulfide to yield the products of partial or complete hydroboration before pyrolysis. These experiments revealed that a minimum boron content (5.7 at.%) and a minimum B/N atomic ratio (0.22) are necessary to protect the ceramic materials from decomposition. Further increasing the boron content has only a minor effect. A second series of experiments, starting from polyvinylsilazane, $[-(H_2C{=}6CH)SiHNH-]_n$, as the polymeric starting material, represents the topic of the present paper.

2. Experimental

2.1. General remarks

The synthetic procedures were performed in a purified argon atmosphere using the Schlenk technique.[24] Borane dimethylsulfide was obtained as a 2 M solution in toluene from Sigma Aldrich GmbH, Germany. Toluene and tetrahydrofurane were purified by distillation from potassium.

Pyrolysis was carried out 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).

Microanalysis 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 porosity of the ceramic specimen was calculated from the bulk density (displacement measurements in mercury), the volume of the ceramic matrix including the closed pores (helium gas pycnometer Accupyc 1300, Micromeritics) and the density of the crushed ceramic powder (helium gas pycnometry).

High temperature TGA of the as-obtained ceramic samples operating a Netzsch STA 501 equipment were carried out in an argon atmosphere (25–1400°C; heating rate $T<1400°C$: 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 rate $T<1400°C$: 10°C/min, $T>1400°C$: 2°C/min, dwell time 5 h) in an argon atmosphere. The X-ray diffraction unit used for the structural investigations of the annealed samples was a Siemens D5000/Kristalloflex (Cu-$K_{\alpha 1}$ radiation), equipped with an OED and a quartz primary monochromator. Samples were milled for 1 h in a WC ball mill before XRD analysis.

2.2. Precursor synthesis

Oligovinylsilazane, $[-(H_2C{=}CH)SiHNH-]_n$ (**1**), was obtained by ammonolysis of vinyldichlorosilane, $(H_2C{=}CH)SiHCl_2$, according to a procedure published by Choong Kwet Yive et al.[25]

In a typical experiment a solution of $H_3B{\cdot}SMe_2$ in 150 ml of toluene was added dropwise to a solution of 20 g (282 mmol) $[-(H_2C{=}CH)SiHNH-]_n$ in 150 ml of toluene at 0°C. The reaction mixture was stirred over night at room temperature. After evaporation of the solvent and SMe_2 in vacuum, the product was dried at 60°C (10^{-2} mbar).

Table 1 gives the different $[-(H_2C{=}CH)SiHNH-]_n/H_3B{\cdot}SMe_2$ molar ratios used for the synthesis of compounds **2–5**.

After the addition of the borane, the solution of **5** transformed into a gel within 15 min. The surface of the reaction mixtures of **3** and **4** was covered with a thin film after several hours, whereas **2** remained dissolved. Removing the volatile components under reduced pressure delivers the polymers as colourless, air- and moisture-sensitive solids in 100% yield. As can be seen from elemental analysis (Table 2), the Si/C/N ratios of the polymers are very similar and the boron content increases constantly.

2.3. Pyrolysis

After ceramization at 1400°C in a flowing argon atmosphere, the ceramic products of **1–5** are black hard solids, which form compact grains with glossy surfaces. In Table 3, the compositions of the as-pyrolysed materials are listed. The ceramics are denoted by the number of the corresponding polymer followed by **c**. As already observed for the polymers, the ceramic materials possess nearly constant Si/C/N ratios and gradually increasing boron contents. However, in comparison with the compositions of the polymeric precursors, the carbon content is reduced significantly by roughly 20%.

Table 1

$[-(H_2C{=}CH)SiHNH-]$(**1**)/$H_3B{\cdot}SMe_2$ molar ratios used for the synthesis of compounds **2–5**

Synthesis of polymer	**2**	**3**	**4**	**5**
$[-(H_2C{=}CH)SiHNH-]/H_3B{\cdot}SMe_2$	8:1	5:1	4:1	3:1
$H_3B{\cdot}SMe_2$ (mmol)	35.3	56.4	70.5	94.0

Table 2
Composition of polymers (wt.%). Calculated values are given in parentheses

	Formula	Si	C	H	N	O	B
1	$[SiC_{2.2}H_{5.1}N_{1.2}]_n$	37.2	34.5	6.8	21.4	n.d.	n.d.
	$([SiC_2H_5N]_n)$	(39.5)	(33.8)	(7.1)	(19.7)	(0.0)	(0.0)
2	$[SiC_{2.0}H_{5.3}N_{0.9}B_{0.13}]_n$	38.6	33.0	7.4	18.2	1.5	2.0
	$([SiC_2H_{5\,{}^{3}/_{8}}NB_{1/8}]_n)$	(38.5)	(33.0)	(7.4)	(19.2)	(0.0)	(1.85)
3	$[SiC_{2.1}H_{5.8}N_{1.1}B_{0.19}]_n$	36.6	32.8	7.6	20.1	1.1	2.7
	$([SiC_2H_{5\,{}^{3}/_{5}}NB_{1/5}]_n)$	(38.0)	(32.5)	(7.6)	(19.0)	(0.0)	(2.9)
4	$[SiC_{1.9}H_{5.9}N_{1.1}B_{0.26}]_n$	36.6	30.2	7.8	20.2	2.0	3.7
	$([SiC_2H_{5\,{}^{3}/_{4}}NB_{1/4}]_n)$	(37.6)	(32.2)	(7.8)	(18.8)	(0.0)	(3.6)
5	$[SiC_{2.0}H_{6.4}N_{1.0}B_{0.35}]_n$	36.6	32.0	8.4	17.8	0.5	4.8
	$([SiC_2H_6NB_{1/3}]_n)$	(37.1)	(31.7)	(8.0)	(18.5)	(0.0)	(4.8)

Table 3
Composition of ceramic materials (wt.%, at.% in parentheses)

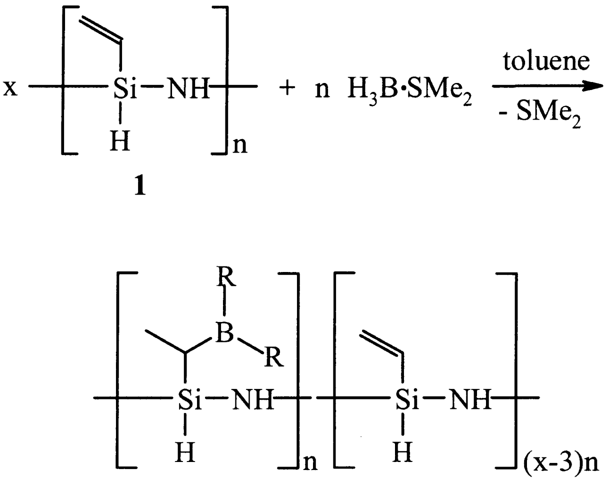
Ceramic	**1c**	**2c**	**3c**	**4c**	**5c**
Si	43.0 (26.8)	42.9 (26.0)	43.0 (26.0)	42.7 (25.3)	41.6 (24.7)
C	29.2 (42.5)	29.6 (41.9)	29.0 (41.0)	29.0 (40.2)	27.6 (38.4)
N	24.3 (30.3)	22.3 (27.1)	22.1 (26.8)	22.1 (26.3)	22.3 (26.6)
O	0.4 (0.4)	1.3 (1.4)	1.1 (1.2)	1.3 (1.4)	1.3 (1.4)
B	–	2.3 (3.6)	3.2 (5.0)	4.5 (6.9)	5.8 (9.0)
Empirical formula[a]	$SiC_{1.6}N_{1.1}$	$SiC_{1.6}N_{1.0}B_{0.14}$	$SiC_{1.6}N_{1.0}B_{0.19}$	$SiC_{1.6}N_{1.0}B_{0.27}$	$SiC_{1.6}N_{1.1}B_{0.36}$

[a] O-content is neglected.

3. Results and discussion

3.1. Synthesis and thermolysis

Oligovinylsilazane **1** was reacted with different amounts of borane dimethylsulfide according to



R=[(C_2H_4)SiH-NH-]

x=8: **2**
x=5: **3**
x=4: **4**
x=3: **5**

C_2H_4: CH_2CH_2 or $CHCH_3$

(3)

The silazane/borane molar ratio was gradually decreased from 8:1 for the synthesis of **2**, 5:1 (compound **3**), 4:1 (compound **4**) up to 3:1 for the preparation of **5**.

By using an excess of oligovinylsilazane for the synthesis of **2**, **3**, and **4**, a part of the vinyl-groups remains intact. Consequently, the polymers are composed of [–$(H_2C{=}CH)$SiHNH–] structural units beside [B(C_2H_4 SiHNH-)$_3$] blocks (C_2H_4: $CHCH_3$, CH_2CH_2). Because of the reactivity of the Si–H bond, further crosslinking by e.g. dehydrocoupling with NH-units with formation of Si–N bonds or hydrosilylation of the olefin units[17] is possible in these systems.[26] Although sol-gel transformations were not observed during hydroboration, the polymers **2–4** are highly viscous and can be handled like solid materials after freeze-drying. For comparison, similar experiments performed with poly(methylvinylsilazane) ($[(H_2C{=}CH)Si(CH_3)NH]_n$) indicated a strong correlation of the boron content and the viscosity of the polymers,[23] probably due to the lower reactivity of the Si–CH_3 bond compared to the Si–H bond.

In contrast to the synthesis of **2**, **3**, and **4** a gelation of the reaction mixture is observed in the synthesis of **5**.[17] The crosslinking by the formation of $(C_2H_4)_3B$-units (C_2H_4: $CHCH_3$, CH_2CH_2) leads to a three-dimensional polymeric network which is exclusively composed of $[B(C_2H_4SiHNH\text{-})_3]_n$ units.

The elemental compositions of **1–5** are listed in Table 2. The measured values are in good accordance with the theoretical values. They mainly differ in the boron contents, whereas the Si/C/N ratio remains within statistical error.

By thermolysis at 1400°C in a flowing argon atmosphere, the polymers **1–5** were transformed into black ceramic materials **1c–5c**, respectively, which possess metallic gloss. While the polymers **1–4** softened during the heat treatment to form big ceramic grains without edges, the polymeric grains of **5** shrinked isotropically with retention of their morphology. The total porosity of the latter ceramic specimens was determined to be 14.7% with an open porosity of 13.6%.

The elemental compositions given in Table 3 show that the ceramization process results in a reduction of the carbon content of about 20%. The Si/C/N ratios, however, are the same for all ceramic materials. Consequently, the only difference in the composition of **1c–5c** is the increasing boron content of 0 at.% in **1c**, 3.6 at.% in **2c**, 5.0 at.% in **3c**, 6.9 at.% in **4c**, up to 9.0 at.% in **5c**.

3.2. High temperature thermogravimetric analysis (HT-TGA)

The results of the high temperature thermogravimetric analysis (1000–2150°C) of the as-pyrolysed materials are shown in Fig. 1. The boron-free material **1c** starts to decompose at 1550°C and loses 24% of its original mass rapidly in a single step. This mass loss corresponds to the amount of nitrogen in the amorphous ceramic material.

By the incorporation of even a small amount of boron in **2c** (3.6 at.%), the beginning of decomposition is shifted up to 1630°C. However, the slope of the mass loss curve and the presence of one single point of inflection indicate that silicon nitride is not stabilized in this material.

Further increasing the boron content to 5.0 at.% in **3c** and 6.9 at.% in **4c** results in a shift of the onset temperature to 1670 and 1700°C, respectively. After a rapid mass loss of 13 (**3c**) and 8% (**4c**), the slope of the curves is significantly reduced at 1870°C. Above this temperature, decomposition reactions proceed at a slow rate.

Material **5c** which possesses the highest boron content in this series shows no signs of spontaneous decomposition during the experiment. Above 1700°C, a very slow but constant mass loss is observed which does not exceed 1% at 1870°C. Above 2000°C, the formation of gaseous species is slightly accelerated leading to a final mass loss of 4.6% at 2150°C.

Based on the compositions of the as-pyrolysed ceramics, the relative phase fractions of the thermodynamically stable phases (at 1400°C) can be calculated.[27]

Table 4
Calculated relative phase fractions of crystalline **1c–5c** materials (at.%, O-content is neglected) and predicted [Δm_p, according to Eq. (2)] and observed mass loss (Δm_o at 1870°C) due to Si_3N_4 decomposition

Ceramic	1c	2c	3c	4c	5c
BN	0	7.3	10.2	14.0	18.2
Si_3N_4	53.3	41.6	38.5	34.2	31.3
SiC	8.1	17.0	19.6	22.2	23.3
C	38.6	34.0	31.7	29.5	27.2
Δm_p	25%	20%	18%	17%	15%
Δm_o	24%	19%	13%	8%	0.8%

Table 5
Calculated BN/Si_3N_4 atomic ratios of materials **2c–5c** after heat treatment at 1870°C

Ceramic	2c	3c	4c	5c
Total sample mass loss at 1870°C	19%	13%	8%	0.8%
$N_{residual}$(1870°C)[a]	15%	41%	64%	96%
$BN_{residual}$/at.%	9.6	12.1	15.5	18.3
$Si_3N_{4residual}$/at.%	0.9	12.7	19.3	29.9
$BN_{residual}/Si_3N_{4residual}$	10.7:1	1.0:1	0.8:1	0.6:1

[a] Of the original nitrogen content.

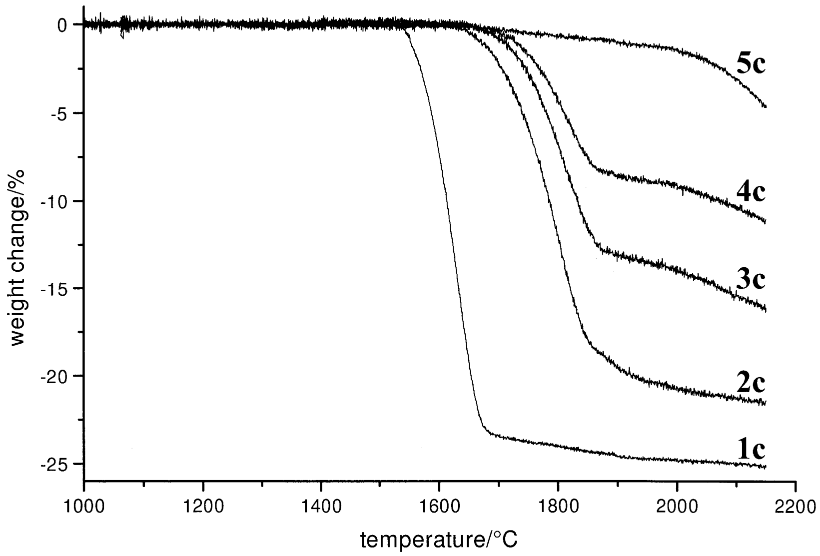


Fig. 1. HT-TGA (1000–2150°C) of ceramic materials **1c–5c** in argon atmosphere (heating rate 10°C/min at $T < 1400°C$ and 5°C at $T > 1400°C$).

The results of these calculations are given in Table 4. Hence, materials **1c–5c** can be compared to hypothetical crystalline composites, composed of boron nitride, silicon nitride, silicon carbide, and carbon. With increasing boron content, the phase fraction of boron nitride increases, thus reducing the amount of nitrogen available for the formation of Si_3N_4. As a consequence, the phase fraction of silicon carbide increases whereas the amount of free carbon decreases.

With regard to the thermal stability of **1c–5c**, Si_3N_4 is the critical compound because of its reaction with carbon at 1484°C with formation of SiC and N_2. Accordingly,

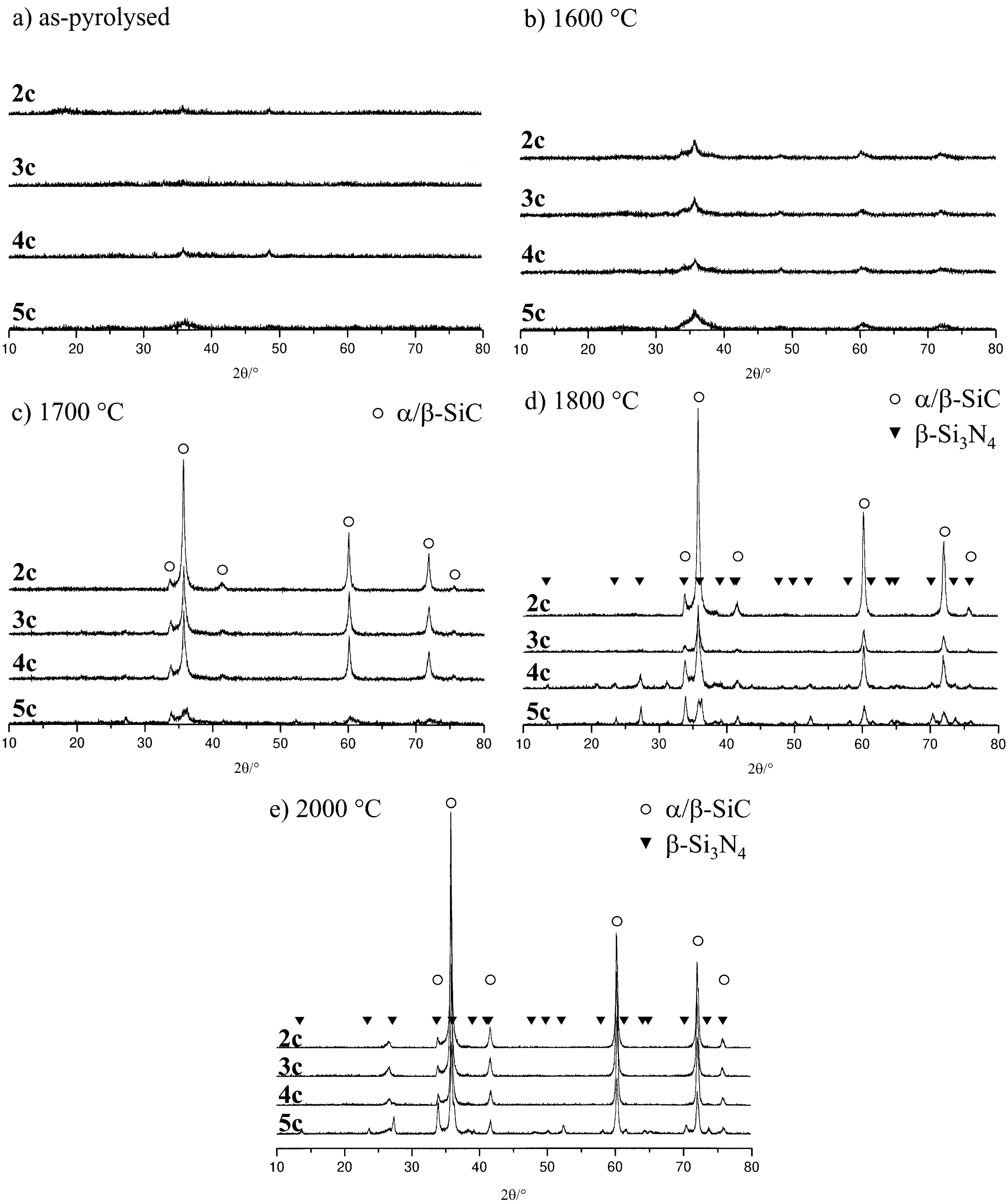


Fig. 2. XRD patterns of (a) as-pyrolysed and (b–e) annealed samples **2c–5c** (annealing time 5 h, argon atmosphere).

excess carbon which is present in all of these materials should lead to a complete decomposition of Si_3N_4 [see Eq. (2)]. The calculated mass loss Δm_p due to N_2 evaporation and the observed values Δm_o are listed in Table 4.

The predicted and observed mass loss at 1870°C are almost identical for the Si–C–N ceramic **1c**, in which the reaction of silicon nitride with carbon occurs quantitatively. Similar observations are made for **2c**. Obviously, the low boron content of 3.6 at.% is not suitable to prevent the complete decomposition of Si_3N_4. In contrast, the difference between the predicted and observed mass loss is significant in materials **3c**, **4c**, and **5c**. This difference increases with increasing boron content.

As mentioned above, the fast mass loss of materials **1c–4c** up to 1870°C is caused by the loss of nitrogen. Consequently, the amount of nitrogen present in the samples decreases continuously during the heat treatment. At 1870°C, material **2c** has lost 85% of its original nitrogen content, whereas in materials **3c**, **4c** and **5c**, the amount of nitrogen is only reduced by 59, 36 and 4%, respectively (Table 5). This change of composition leads to ceramic materials which are stable at higher temperatures; the decomposition of Si_3N_4 (still present in **3c**, **4c** and **5c**) is effectively retarded above 1870°C. Based on the nitrogen loss determined by TGA, the compositions of these stable ceramics can be calculated (Table 5). As a result, the atomic ratio BN/Si_3N_4 is not constant in these materials but decreases disproportionately with increasing Si_3N_4 content. That is, to stabilize double the amount of Si_3N_4, the quantity of BN need increase by a factor of only 1.5.

3.3. X-ray diffraction (XRD) studies

In order to investigate the crystallization behaviour and phase evolution, the as-pyrolysed ceramic materials **2c–5c** were annealed at different temperatures for 5 h each in an argon atmosphere.

After pyrolysis at 1400°C, the materials are X-ray amorphous (Fig. 2a). The beginning of crystallization at about 1600°C (Fig. 2b) is indicated by very broad SiC-diffraction peaks whereas the half width of the signals is already reduced in the diagrams of **2c–4c** in comparison with **5c**. This difference is clearly distinct in the XRD patterns after annealing the samples at 1700°C (Fig. 2c). Material **5c** still shows very broad peaks for SiC indicating a hindered crystallization. Furthermore, weak signals attributable to β-Si_3N_4 can also be detected. In contrast, the diagrams of **2c–4c** are very similar and reveal a higher crystallinity of these materials. The specimens **3c** and **4c** mainly consist of silicon carbide although a small amount of silicon nitride is present, whereas Si_3N_4 is completely absent in material **2c**. At 1800°C the samples are predominantly crystalline. The diagrams of **2c** and **3c** correspond to the diffraction pattern of silicon carbide. In the boron-richer materials **4c** and **5c**, Si_3N_4-reflections are distinctly detected beside SiC-peaks. At 2000°C finally, the thermodynamically expected cleavage of Si-N bonds proceeds in **4c** resulting in the absence of Si_3N_4-peaks in the XRD-diagram. Material **5c** which proved to be the only thermally stable composite in this series (see thermogravimetric analysis) still contains crystalline silicon carbide and silicon nitride.

All samples heat-treated at 2000°C exhibit an additional broad reflection at 26.6°, which is characteristic for graphitic carbon.

4. Summary and conclusions

Hydroboration of oligovinylsilazane $[-(H_2C{=}CH)SiHNH-]_n$ with different amounts of $H_3B{\cdot}SMe_2$ delivers polymers with a nearly constant Si/C/N atomic ratio but different B/Si atomic ratios. Thermolysis of these polymers at 1400°C results in amorphous ceramics. The relative amounts of silicon, nitrogen and boron are not affected by this process, they remain constant. In contrast, the carbon content is reduced in all materials by roughly 20%. Remarkably, the pyrolysis of similar polymers with Si–CH_3 groups instead of Si-H groups leads to ceramic materials with an identical C/Si ratio of 1.6,[23] indicating an easy cleavage of the Si–CH_3 bond and removal of methane under thermic stress.

High temperature thermogravimetric analysis reveals an increasing thermal stability of the ceramic materials with increasing boron content. It is observed that a minimum of 9 at.% boron is necessary to efficiently protect the materials from thermal degradation. This value is significantly higher than the value observed in a previous study dealing with Si-methylated precursors (5.7 at.%), although the Si/C/N ratios are similar in both systems. Consequently the differences are probably due to a change of the microstructure that is formed during pyrolysis.

XRD studies confirm the results of the high temperature thermogravimetric analysis. In material **2c** the small amount of incorporated boron has no effect on the stabilization of silicon nitride which decomposes during crystallization at 1700°C. As a consequence of further increasing the temperature, crystalline Si_3N_4 present in **3c** and **4c** decomposes at temperatures below 1800 and 2000°C, respectively.

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