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

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Abstract

The preparation and characterization of precursor derived Si–B–C–N ceramics with similar Si/C/N ratios but variable boron content are reported. The polymeric precursors were prepared via hydroboration of poly(methylvinylsilazane) using different BH₃·SMe₂/polymer stoichiometries. High temperature thermogravimetric analysis of as-pyrolysed ceramics as well as XRD studies of post-annealed samples display a retarding effect of boron on both crystallization of SiC and Si₃N₄ and stabilization of crystalline β -Si₃N₄. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Within this decade precursor-derived Si-B-C-N ceramics became of topical interest because of their extraordinary high temperature stability.^{1–3} Recently developed materials withstand temperatures up to 2000°C for several hours without any sign of decomposition, although crystallization starts at about 1700–1800°C.^{4–11} XRD studies of selected samples revealed the presence of SiC and Si₃N₄ after annealing at 2000°C for several hours,¹² even though silicon nitride is chemically not stable at this temperature due to either reaction with carbon [1484°C at 1 atm. N₂; Eq. (1)] or to decomposition into the elements [1841°C at 1 atm. N₂; Eq. (2)] according to the following reactions¹³.

$$Si_3N_4 + 3C \longrightarrow 3SiC + 2N_2 \uparrow$$
 (1)

$$Si_3N_4 \longrightarrow 3Si + 2N_2 \uparrow$$
 (2)

These reactions are usually observed on heating ternary Si–C–N ceramics to elevated temperatures.

Although the extension of the Si–C–N system with boron generally improves the high temperature stability of the respective ceramics, a number of Si-B-C-N materials is

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known, which start to decompose between 1600 and 1800° C.^{14–16} The comparison of the composition of different Si–B–C–N ceramics points to the fact that materials with a low (<3 wt.%) or a high (16–18 wt.%) boron content are less well protected from thermal degradation.

An important detail, which is more difficult to quantify, is the influence of the structure of the precursors on the thermal stability of precursor derived ceramics. However, a homogeneous elemental distribution on the molecular scale is a prerequisite. In contrast, partial demixing in the Si–B–C–N precursor during pyrolysis, e.g. by formation of borazine units, causes the formation of multiphase composites which decompose in the thermodynamically expected temperature range.^{17–20}

Some models have been developed to explain the role of boron with respect to the high temperature behaviour of Si–B–C–N ceramics.^{12,21} Theories are generally based on the reduced mobility of atomic species in the amorphous state. Crystalline segregations (Si₃N₄, in particular) are possibly protected from decomposition by a turbostratic BN phase that can be built at elevated temperatures. Such phases possibly increase local nitrogen pressure and shift decomposition reactions according to (1) and (2) to higher temperatures.^{21–23} Furthermore, it is supposed that carbon is incorporated into the BN phase and thus its activity is reduced. However, the reasons for high temperature stability are not unequivocally understood until now.

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In order to gain more insight into both the kinetics and thermodynamics of the Si–B–C–N system, this systematic study was carried out, starting with poly(methylvinylsilazane) which was modified by reaction with different amounts of borane dimethylsulfide.

2. Experimental

2.1. General remarks

The synthetic procedures were performed in a purified argon atmosphere using the Schlenk technique.^{†,25} Poly(methylvinylsilazane) **1** was obtained according to the literature.²⁶ Borane dimethylsulfide was obtained as a 2 M solution from Sigma Aldrich GmbH, Germany. Toluene was 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).

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).

High temperature thermal gravimetric analysis (HTTGA) of the as-obtained ceramic samples operating a Netzsch STA 501 equipment was 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 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.

2.2. Precursor synthesis

In a typical experiment a solution of $H_3B \cdot SMe_2$ in 150 ml of toluene was added dropwise to 20 g [-MeSi(Vi) NH-]_n (1, 235 mmol) dissolved in 150 ml of toluene at 0°C. The reaction mixture was stirred for 12h at room temperature. After removing the solvent and SMe₂ in vacuum, the air and moisture sensitive product was dried at 60°C (10⁻² mbar). Table 1 gives the different [-MeSi(Vi)NH-]/H₃B·SMe₂ molar ratios which were used for the synthesis of compounds **2–5**.

The hydroboration reaction occurred quantitatively. The viscosity of the colourless polymers increased with increasing boron content (starting compound 1: oily liquid, 2: viscous oil, 3: highly viscous oil, 4: soft solid, 5: glass-like material).

2.3. Pyrolysis

The ceramization does not cause significant change in the Si/B/N ratio of the materials, whereas the relative carbon content decreases significantly but independently of the boron content. The results of the elemental analysis of the ceramics (marked by the number of polymer followed by \mathbf{c} for ceramic) are listed in Table 3.

3. Results and discussion

3.1. Synthesis and pyrolysis

Poly(methylvinylsilazane) was reacted with different amounts of borane dimethylsulfide according to



Table 1

 $[-MeSi(Vi)NH–](1)/H_3B\cdot SMe_2$ molar ratios used for the synthesis of compounds 2--5

Polymer	2	3	4	5
[-MeSi(Vi)NH-]/H ₃ B·SMe ₂	8:1	5:1	4:1	3:1
H ₃ B·SMe ₂ (mmol)	29.6	46.8	56.4	78.2

Table 2	
Composition	of polymers ^a

	Theoretical formula	Si	С	Н	Ν	0	В
1	$[SiC_{3.0}H_{6.9}N_{1.0}]_n$ $([SiC_3H_7N]_n)$	32.9 (33.0)	41.8 (42.3)	8.1 (8.3)	16.8 (16.4)	0.8 (0.0)	0.0 (0.0)
2	$\begin{array}{l} [\mathrm{SiC}_{3.0}\mathrm{H}_{6.4}\mathrm{N}_{1.0}\mathrm{B}_{0.14}]_n \\ ([\mathrm{SiC}_3\mathrm{H}_{7_{3/8}}\mathrm{NB}_{1/8}]_n) \end{array}$	31.8 (32.3)	40.4 (42.3)	7.3 (8.6)	15.7 (16.1)	1.0 (0.0)	1.7 (1.6)
3	$\begin{array}{l} [\mathrm{SiC}_{3.2}\mathrm{H}_{7.6}\mathrm{N}_{1.1}\mathrm{B}_{0.23}]_n \\ ([\mathrm{SiC}_3\mathrm{H}_{7_{3/5}}\mathrm{NB}_{1/5}]_n) \end{array}$	29.7 (31.9)	40.8 (41.0)	8.1 (8.7)	17.0 (15.9)	1.2 (0.0)	2.6 (2.5)
4	$\begin{array}{l} [{\rm SiC}_{3.0}{\rm H}_{7.3}{\rm N}_{1.0}{\rm B}_{0.26}]_n \\ ([{\rm SiC}_3{\rm H}_{7_{3/4}}{\rm NB}_{1/4}]_n) \end{array}$	31.1 (31.7)	40.0 (40.7)	8.2 (8.8)	15.3 (15.8)	2.1 (0.0)	3.1 (3.0)
5	$[\text{SiC}_{3.1}\text{H}_{7.6}\text{N}_{1.0}\text{B}_{0.35}]_n \\ ([\text{SiC}_3\text{H}_8\text{NB}_{1/3}]_n)$	30.5 (31.3)	40.4 (40.1)	8.3 (9.0)	15.3 (15.6)	1.7 (0.0)	4.1 (4.0)

^a wt.%, calculated values in parenthesis.

[†] This preparative method is based on experiments developed by the German chemist Wilhelm Schlenk. All apparatus are equipped with sidearms for pumping out the air and moisture and introducing inert gas.

Ceramic	1c	2c	3c	4c	5c
Si	45.4 (27.6)	44.7 (27.2)	43.2 (25.6)	42.0 (25.0)	41.9 (24.5)
С	31.4 (44.6)	28.1 (39.9)	30.3 (42.0)	29.8 (41.4)	29.8 (40.7)
Ν	22.3 (27.1)	22.6 (27.5)	21.3 (25.3)	21.0 (25.0)	20.6 (24.2)
0	0.7 (0.7)	1.2 (1.3)	1.4 (1.5)	1.6 (1.7)	1.6 (1.6)
В	_	2.6 (4.1)	3.7 (5.7)	4.5 (6.9)	5.9 (9.0)
Empirical formula ^b	$\mathrm{SiC}_{1.6}\mathrm{N}_{1.0}$	$SiC_{1.5}N_{1.0}B_{0.15}$	$SiC_{1.6}N_{1.0}B_{0.22}$	$SiC_{1.7}N_{1.0}B_{0.28}$	SiC _{1.7} N _{1.0} B _{0.37}

Table 3 Composition of as-pyrolysed materials^a

^a wt.%, at.% in parenthesis

^b O-content is neglected.

The polymer was dissolved in toluene and borane dimethylsulfide added drop-wise. The polysilazane: borane molar ratios were 8:1 (compound 2), 5:1 (compound 3), 4:1 (compound 4) and 3:1 (compound 5). The latter reaction represents the case of quantitative hydroboration yielding a polymer with only $[B(C_2H_4)Si-(CH_3)NH]$ structural units,¹² whereas compounds 2–4 are composed of $[(H_2C=CH)Si(CH_3)NH]$ and $[B(C_2H_4)Si-(CH_3)NH]$ building blocks. The hydroboration of 1 causes its cross-linkage, which is directly reflected in increasing polymer viscosity with increasing boron content. While pure 1 is a liquid, 2 and 3 are viscous oils, 4 is a waxy solid and 5 is a glass-like material. The Si/C/N ratio in the polymers is not affected by this reaction (see Table 2).

Pyrolysis of 2–5 in argon atmosphere delivers ceramic materials 2c-5c as black solids with metallic gloss. Their compositions, which are given in Table 3, are located within the same compositional space constituted by BN, Si_3N_4 , SiC and C. Since the Si/C/N ratio in the precursor-derived ceramics is not affected by the amount of boron incorporated in the precursor, the high temperature characteristics of 2c-5c can be attributed to the presence of a different amount of boron solely.

3.2. High temperature thermogravimetric analysis

The results of the high temperature thermogravimetric analysis of the ceramics 1c-5c are shown in Fig. 1. It is observed that the stability towards thermal decomposition strongly depends on the boron content. Both the boron-free 1c as well as the material 2c which contains 2.4 wt.% B, start to decompose at about 1600 and 1650°C, respectively. While 1c decomposes in a single reaction step with a weight loss of 25%, there is a two step decomposition observed for 2c. In the first step, a rapid weight loss of 7% occurs. In contrast, further decomposition progress, initiated at 1830°C, proceeds slower. The total value at 2150°C is about 9.8%.

The materials 3c and 4c are subject to a continuous weight loss starting at about 1600°C in one single reaction

step very similar to the one observed for 2c in this temperature range. The boron-richer ceramic 4c (4.5 wt.% B) is somewhat more stable than 3c (3.7 wt.% B). At 2000°C the respective weight losses are 1.4 and 2.1%, while at 2150°C these values are more than doubled to 3.0 and 4.5%.

Material **5c** shows no mass change up to 1800° C. At 2000°C, the weight loss does not exceed 1%. Further heat treatment leads to decomposition with a decrease in weight similar to that observed for **3c** and **4c**.

According to thermodynamic calculations based on the CALPHAD method²⁷ the stable binary phases in the Si–B–C–N system up to 1484°C are BN, Si₃N₄, SiC and C, assuming a total pressure of 1 bar.²⁸ At higher temperatures a reaction of Si₃N₄ with carbon under the formation of SiC and N₂ (gas) is predicted. From the calculated phase fractions of **1c–5c** which are given in Table 4) the theoretical weight loss due to the evaporation of N₂ can be calculated. Surprisingly, in the case of the boron containing ceramics the calculated values which decrease in the row **1c→5c** are always significantly higher than those observed in the TGA experiment. In contrast, the calculated (23%) and



Fig. 1. HT-TGA (400–2150°C) of ceramic materials 1c to 5c with magnified plot of 2c to 5c at temperatures $> 1400^{\circ}C$ (inset).

Table 4 Calculated relative phase fractions (at.%, O content is neglected) and predicted $[\Delta m_p$, according to Eq. (2)]/observed mass loss (Δm_o) due to Si₃N₄ decomposition at 1840°C

Ceramic	1c	2c	3c	4c	5c
BN	0.0	8.3	11.6	15.1	18.2
Si ₃ N ₄	47.9	41.5	34.8	29.7	27.0
SiC	14.5	19.5	22.1	24.5	26.7
С	37.6	30.7	31.5	30.7	28.1
$\Delta m_{\rm p}$ (%)	23	20	17	14	13
$\Delta m_{\rm o}^{\rm P}$ (%)	25	7	1	0.5	0

observed weight losses (25%) in the case of the boronfree ceramic **1c** are almost identical.

From Table 4, it can further be concluded that all possible subsystems should be present in 2c-5c. With increasing boron content the relative phase amount of BN increases from 8.3% in 2c to 18.2% in 5c, whereas the relative amount of Si₃N₄ decreases. Consequently, the Si₃N₄/BN ratio decreases significantly with increasing boron content from 5.0 in 2c to 3.0 in 3c, 2.0 in 4c, and 1.5 in 5c. On the assumption that the weight loss of 2c up to 1830°C is only caused by generation of N₂ the Si₃N₄/BN ratio of the residue amounts to 3.2, i.e. the N/B ratio is 1/0.22 which is the same for as pyrolysed material 3c.

3.3. XRD-studies

The as-pyrolysed ceramic materials are X-ray amorphous (see Fig. 2a). Bragg reflections can be detected after annealing for 5 h at 1600, 1700 and 2000°C.

At 1600°C (Fig. 2b), very broad reflections indicate beginning crystallization of SiC, whereas Si_3N_4 reflections cannot be detected. The line-width of peaks is very similar for **3c–5c** where as it decreases significantly in the case of **2c**.

After annealing at 1700°C (Fig. 2c) SiC- and β -Si₃N₄ reflections are found for every ceramic material, though in different ratios. In **2c**, only traces of crystalline Si₃N₄ are present whereas the respective reflections in **3c**, **4c** and **5c** are clearly stronger. Generally, the peak intensities of SiC and Si₃N₄ decrease in the row **2c** \rightarrow **5c**, indicating hindered crystallization with increasing boron content. This order is not rigid, though, since the peak intensities of **4c** are a little weaker than those of **5c**.

At 2000°C (Fig. 2d), the different compositions of 3c, 4c and 5c versus that of 2c are more obvious While the XRD pattern of the former materials, which proved excellent thermal stability in the TGA experiment (Fig. 1), exhibit characteristic SiC and Si₃N₄ reflections, silicon nitride reflections completely vanished in 2c material. In addition, the XRD plots of 3c and 4c are very



Fig. 2. XRD of (a) as-obtained and (b)-(d) annealed samples 2c-5c (annealing time 5 h, argon atmosphere).

similar with regard to the peak intensities. Again the reflections of **5c** are weaker while **2c** shows the strongest reflections.

4. Summary and conclusions

Thermolysis of boron-modified poly(methylvinylsilazane) delivers Si–B–C–N ceramics whose thermal stabilities are dependent on the boron content. While the boron-free material decomposes at about 1500°C, the modification with 2.6 wt.% of boron results in a stabilization towards thermal degradation up to 1650°C. Further increasing the amount of boron to finally 5.9 wt.% results in a shift of the decomposition temperature to approximately 1900°C. This shift of the decomposition temperature to higher temperature is reflected in the XRD experiments. The tendency for a crystallization of the as-obtained amorphous materials decreases with increasing boron content.

To explain the effect of boron on the high temperature stability in this Si–B–C–N system sufficiently, two distinct phenomena have to be taken into account:

- 1. Boron stabilizes the amorphous state in these Si–B–C–N ceramics. As a result of hindered crys-tallization less and/or smaller crystallites are formed.
- 2. Si₃N₄, thermodynamically not stable at elevated temperatures, is protected against decomposition. To prevent silicon nitride decomposition efficiently a certain relative amount of boron is necessary. If it is too low relative to the amount of silicon nitride, the material probably releases nitrogen until the B/N ratio is about 0.22. This ratio seems to be the minimum necessary for obtaining high temperature stable ceramics in this system.

To assess the full significance of the observed phenomena, further studies are required. Transmission electron microscopy should supply indications about the microstructure, in particular the amount and composition of amorphous and crystalline phases.

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