

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

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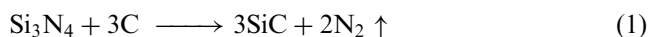
Abstract

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 $\text{BH}_3\cdot\text{SMe}_2$ /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 Si_3N_4 and stabilization of crystalline β - Si_3N_4 . © 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 Si_3N_4 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. N_2 ; Eq. (1)] or to decomposition into the elements [1841°C at 1 atm. N_2 ; Eq. (2)] according to the following reactions¹³.



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

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 (Si_3N_4 , 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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Table 3
Composition of as-pyrolysed materials^a

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)
C	31.4 (44.6)	28.1 (39.9)	30.3 (42.0)	29.8 (41.4)	29.8 (40.7)
N	22.3 (27.1)	22.6 (27.5)	21.3 (25.3)	21.0 (25.0)	20.6 (24.2)
O	0.7 (0.7)	1.2 (1.3)	1.4 (1.5)	1.6 (1.7)	1.6 (1.6)
B	–	2.6 (4.1)	3.7 (5.7)	4.5 (6.9)	5.9 (9.0)
Empirical formula ^b	SiC _{1.6} 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}

^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(C₂H₄)Si(CH₃)NH] structural units,¹² whereas compounds **2–4** are composed of [(H₂C=CH)Si(CH₃)NH] and [B(C₂H₄)Si(CH₃)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, Si₃N₄, 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-rich 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

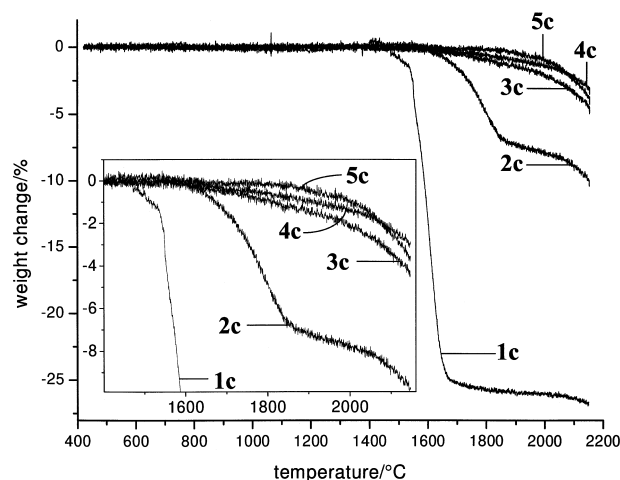


Fig. 1. HT-TGA (400–2150°C) of ceramic materials **1c** to **5c** with magnified plot of **2c** to **5c** at temperatures > 1400°C (inset).

Table 4

Calculated relative phase fractions (at.%, O content is neglected) and predicted [Δm_p , according to Eq. (2)]/observed mass loss (Δm_o) due to Si_3N_4 decomposition at 1840°C

Ceramic	1c	2c	3c	4c	5c
BN	0.0	8.3	11.6	15.1	18.2
Si_3N_4	47.9	41.5	34.8	29.7	27.0
SiC	14.5	19.5	22.1	24.5	26.7
C	37.6	30.7	31.5	30.7	28.1
Δm_p (%)	23	20	17	14	13
Δm_o (%)	25	7	1	0.5	0

observed weight losses (25%) in the case of the boron-free 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 Si_3N_4 decreases. Consequently, the $\text{Si}_3\text{N}_4/\text{BN}$ 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 N_2 the $\text{Si}_3\text{N}_4/\text{BN}$ 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 $\beta\text{-Si}_3\text{N}_4$ reflections are found for every ceramic material, though in different ratios. In **2c**, only traces of crystalline Si_3N_4 are present whereas the respective reflections in **3c**, **4c** and **5c** are clearly stronger. Generally, the peak intensities of SiC and Si_3N_4 decrease in the row **2c**→**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 Si_3N_4 reflections, silicon nitride reflections completely vanished in **2c** material. In addition, the XRD plots of **3c** and **4c** are very

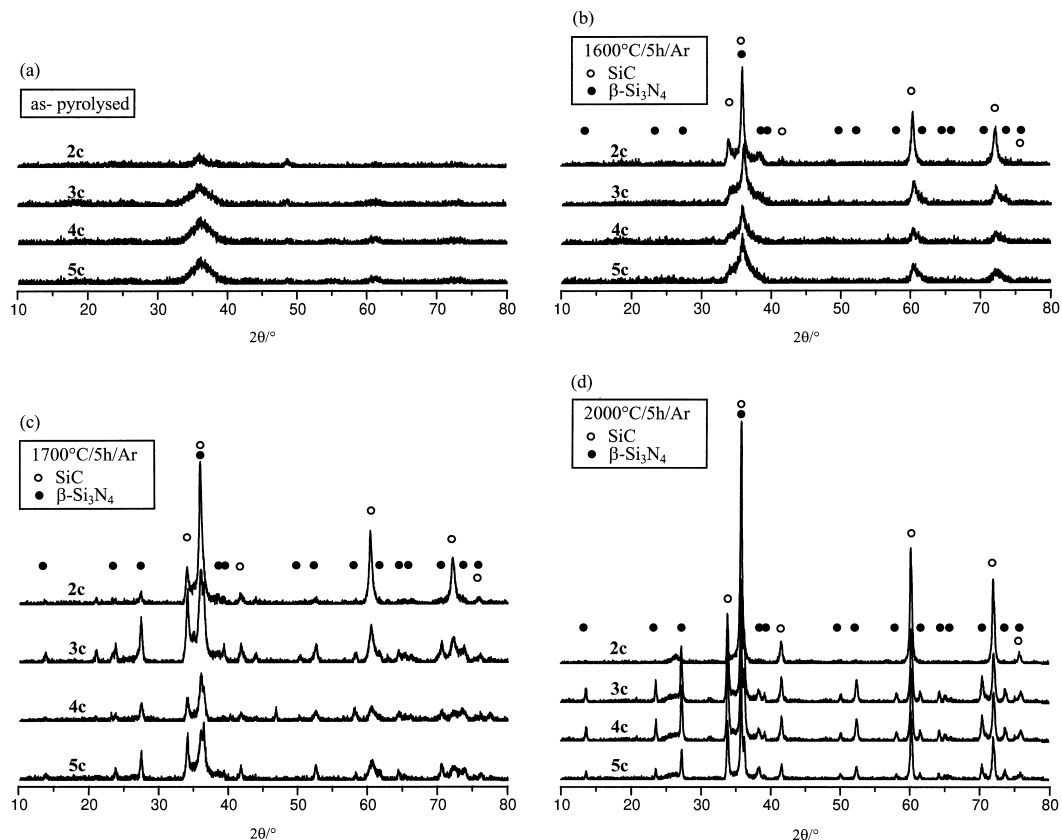


Fig. 2. XRD of (a) as-obtained and (b)–(d) annealed samples **2c–5c** (annealing time 5 h, argon atmosphere).

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 crystallization 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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