

In-Situ Carbon Content Adjustment in Polysilazane Derived Amorphous SiCN Bulk Ceramics

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Abstract

The present paper is concerned with the *in-situ* carbon content adjustment in amorphous bulk silicon carbonitride (SiCN) ceramic matrices prepared by the polymer to ceramic transformation of cross-linked and compacted poly(hydridomethyl)silazane powders. Heat treatment in inert (Ar) or reactive atmosphere (ammonia, or mixed Ar/NH₃ with different volume ratio of ammonia) was used for carbon content adjustment. Isothermal annealing steps in Ar and/or mixed atmospheres at various intermediate temperatures were also included into the pyrolysis schedule (i) to adjust the final carbon content, (ii) to control outgassing of low molecular reaction products like methane or hydrogen from the matrix during polysilazane decomposition and thus (iii) to avoid cracking of the pressed polymer powders. Optimal annealing temperature for carbon content adjustment was found to be in the range between 500 and 550°C. Increasing NH₃ contents from 10 to 50 vol% in the pyrolysis atmosphere as well as enhanced transient annealing temperature and time promote carbon reduction. In contrast intermediate isothermal annealing in Ar at 500 up to 600°C results in pronounced formation of Si–C bonds and in increased carbon contents after the final pyrolysis process. Depending on the pyrolysis conditions, flawless bulk specimens with carbon contents ranging from 0.3 up to 16.2 wt% were obtained. Different possible chemical reactions are considered

to explain the generation of the particular Si(C)N compositions found. © 1999 Elsevier Science Limited. All rights reserved

Keywords: amorphous ceramics, precursors, organic, carbon, Si₃N₄, SiC.

1 Introduction

Ceramics based on silicon nitride and silicon carbide are candidate materials for high temperature applications. However, metal oxides like Al₂O₃ or Y₂O₃ have to be added to the matrix powders to obtain fully dense ceramics. One main drawback of the conventionally processed silicon nitride and carbide based ceramics is that the metal oxide phases limit the maximum temperature at which the sintered material can be used. It was reported in recent years that organosilicon polymers like polysilazanes offer the opportunity to prepare silicon nitride and silicon carbonitride bulk ceramics without addition of metal oxides.^{1–4} Therefore, improved high temperature properties and oxidation resistance of these additive-free SiCN ceramics can be expected.⁵ In the course of our work we found that silicon carbonitride ceramics with the composition Si₁C_{0.58}N_{0.90} remain amorphous up to 1400°C in argon or nitrogen and 1500°C in air.⁵

However, at higher temperatures the non-stoichiometric Si₁C_{0.58}N_{0.90} matrix decomposes and partitions by the loss of nitrogen to give the thermodynamically stable phases, namely Si₃N₄ and SiC.^{6–8} This finding is illustrated by the ternary SiCN phase diagram as shown in Fig. 1. The polysilazane-derived ceramics of the general composition A, Si_{3+x}C_{x+y}N₄, remains metastable at

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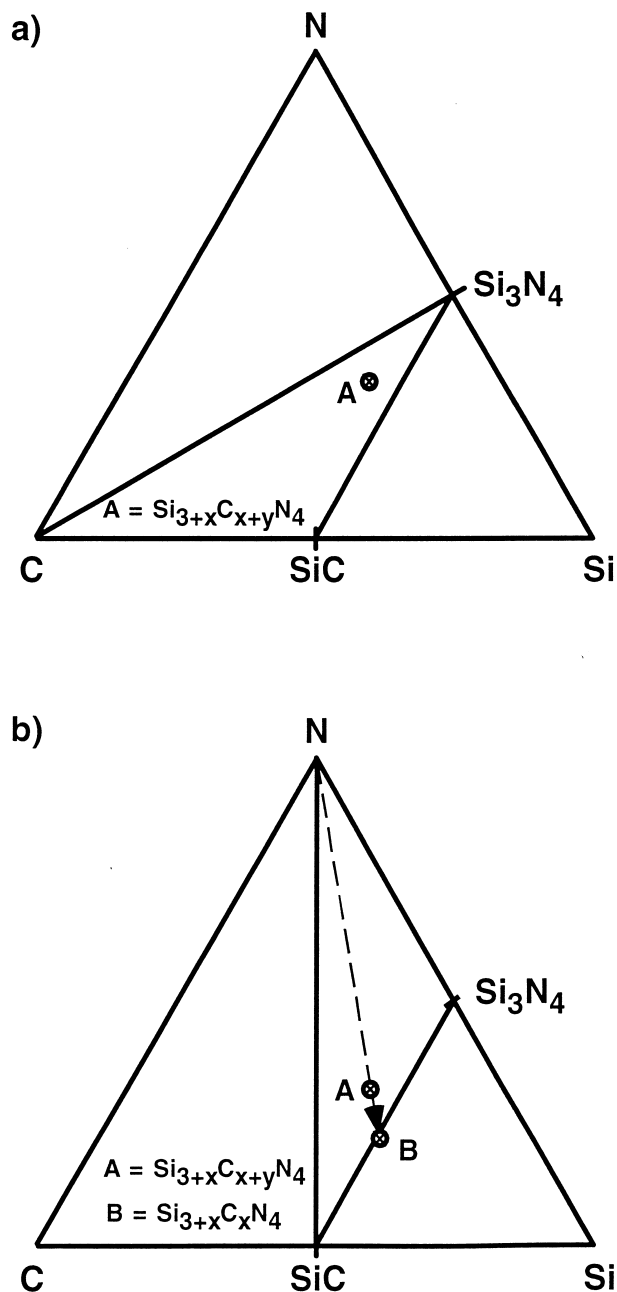


Fig. 1. Schematic illustration of amorphous poly(hydrido-methyl)silazane derived SiCN after pyrolysis at (a) $T \leq 1440^\circ\text{C}$ and (b) its crystallisation path at $T > 1440^\circ\text{C}$,⁹ in respective isothermal sections of the ternary SiCN phase diagram. Compositions are given in atom% and the oxygen content in amorphous SiCN is neglected.

$T < 1440^\circ\text{C}$ and gives off nitrogen at $T > 1440^\circ\text{C}$ as long as the system reaches the tie line composition B, $\text{Si}_{3+x}\text{C}_x\text{N}_4$, and finally crystallises to give Si_3N_4 and SiC. Consequently, the thermal stability of SiCN regarding degradation should be significantly enhanced by avoiding nitrogen evolution in the high temperature region. This, however, requires the direct formation of $\text{Si}_{3+x}\text{C}_x\text{N}_4$ compositions by the polymer to ceramic transformation. Therefore, the present work reports on the carbon content adjustment by the reactive heat treatment of poly(hydrido-methyl)silazanes in mixed NH_3/Ar atmospheres and emphasises the synthesis of

amorphous Si(C)N bulk ceramics with precisely tailored carbon contents. Possible formal reactions contributing to the formation of the Si(C)N ceramics during the polymer to ceramic conversion are discussed.

2 Experimental Procedure

All experiments were performed with commercially available poly(hydrido-methyl)silazane NCP200, $[(\text{CH}_3)_2\text{SiNH}]_x[(\text{CH}_3\text{SiHNH})_y][\text{CH}_3\text{SiN}]_z$ with $x = y = z$, distributed by Nichimen Corp., Tokyo, Japan. The precursor is an agglomerated powder with an approximate chemical composition of $\text{Si}_{1.0}\text{C}_{1.5}\text{N}_{1.0}\text{H}_{5.5}$. Due to its oxygen and moisture sensitivity, the polysilazane was manipulated and stored in a glove box under argon (99.999% purity). Argon and NH_3 with 99.999% purity (Linde AG, Germany) were used during the specimen preparation as inert and reactive gas.

2.1 Cross-linking

A batch of 30 g of polysilazane was filled into a quartz tube and cross-linked in a vertical tube furnace with SiC heating elements (Gero, model HTSR 40-200, temperature measured by Pt-PtRh10 thermocouple). The precursor was heated at 600°C h^{-1} in flowing argon (gas flow $6\text{ dm}^3\text{ h}^{-1}$, controlled by Brooks 5850 flow rate controller) up to 350 or 600°C ; the annealing time at this temperature was 2 or 3 h (Table 1). At the end of the cross-linking step the quartz tube was evacuated for 1 h at the respective temperature to remove oligomeric compounds from the product and then quenched to room temperature. The cross-linking was controlled by measuring the weight loss and the polymer softening by quantitative thermal analysis using TGA and TMA. Thermal gravimetric analysis (TGA) was carried out on a Netzsch STA 429 in flowing Ar in the temperature range between 25 and 1000°C with a heating rate of 300°C h^{-1} . Thermal mechanical analysis (TMA) was performed on Netzsch TMA 402 equipment using identical conditions.

2.2 Pressing, transient annealing and pyrolysis

Cross-linked polysilazane was milled in air-tight high-density polyethylene jar with zirconia milling balls for 8 h and sieved through a $32\ \mu\text{m}$ screen. The powder was filled into cylindrical dies made of silicon latex and cold isostatically pressed (CIP) at 200 or 500 MPa. The as-received cylindrical bodies with 22 mm in diameter and 15 mm in height were placed in a quartz tube and pyrolysed in a horizontal tube furnace with SiC heating elements at 1000 or 1100°C for 4 h with a heating rate

Table 1. Heating schedule used for the cross-linking of the poly(hydridomethyl)silazane

Sample	Heating schedule	Degree of cross-linking
A	600°C/h→350°C/2 h(Ar) + 1 h(vac)	Under-cross-linked
B	600°C/h→350°C/3 h(Ar) + 1 h(vac)	Optimal
C	600°C/h→600°C/2 h(Ar) + 1 h(vac)	Over-cross-linked

of 25°C h⁻¹. For most of the specimens an isothermal annealing at a transient temperature of 500, 525, 550 or 600°C lasting between 5 and 25 h was included into the pyrolysis procedure (Table 2). In the temperature interval between 400 and 900°C the evolution of gaseous reaction products, CH₄ and H₂, was observed.^{1,4} Therefore, the isothermal heat treatment at these intermediate temperatures was applied (i) to effectively influence the decomposition reactions by the furnace atmosphere as well as (ii) to control outgassing of the volatile by-products and thus to avoid crack formation during pyrolysis caused by rapid gas evolution. Figure 2 demonstrates the polysilazane processing and the different annealing procedures used for the Si(C)N sample preparation.

All pyrolysis experiments were performed either in inert (Ar, 99.999% purity, flow rate 6 dm³ h⁻¹) or reactive atmosphere (mixture of Ar and NH₃ with 10, 22 or 50 vol% of NH₃ or pure NH₃; gas flow 6 dm³·h⁻¹). The pyrolysed pellets were furnace cooled to room temperature. Shrinkage and weight loss of the specimens were determined. The sample notations, their heat-treatment schedules and the measured Si(C)N-compositions after pyrolysis under various conditions applied here are summarised in Tables 2–4.

2.3 Characterisation

The pore size distribution and open porosity were analysed by mercury pressure porosimetry with a

Micromeritics Poresizer model 9320, before and after pyrolysis of the compacted polysilazanes. The results were compared with those obtained from the density measurements. The skeletal density of the obtained Si(C)N material was measured by pycnometry in dried cyclohexane. To avoid soaking, several pieces were coated with a thin polymeric layer and the bulk density was then measured by the Archimedes method in water.

Parts of the specimens were crushed in an agate mortar and used for XRD examination and elemental analysis. X-ray diffraction (XRD) measurements were performed for 2 θ angle (20°, 85°) with CuK α radiation, using a Siemens D5000 diffractometer operating at 25 kV. The weight fractions of C, N and O in the specimens were measured by a Leco EC12 carbon determinator and Leco TC436 N/O determinator, respectively. For each specimen the C, N and O contents from the centre of the cylindrical compact as well as from near surface were analysed. The weight fraction of silicon in the specimens was calculated as the difference of the sum of the measured C, N and O weight fractions to 100%. Since the hydrogen content in pyrolysed specimens usually does not exceed 1 wt%,¹⁰ this calculation yields a result which is within the range of experimental error of the measuring equipment.

3 Results and Discussion

3.1 Polymer to ceramic conversion

Heat treatment of the poly(hydridomethyl)silazane in Ar or NH₃ yields Si(C)N materials with different chemical compositions. The changes in weight and density during the pyrolysis of polysilazanes is schematically shown in Fig. 3. Pyrolysis in argon at 1000–1100°C results in an amorphous product, Si_{1.0}C_{0.58}N_{0.90}¹⁰ while carbon-free specimens with the composition close to that of stoichiometric

Table 2. Heating treatment, weight loss, density and empirical formulae of powder B cold-isostatically pressed at 200 MPa and subsequently pyrolysed in Ar, NH₃ or Ar/NH₃ (10 vol%) atmospheres without annealing at a transient temperature prior to pyrolysis. The empirical formula of the pyrolysed specimens are derived from the C/N/O elemental analysis data

Sample	Heat treatment	Δm^a (%)	ρ^b (g cm ⁻³)	ρ_T^c (g cm ⁻³)	ρ^d (%)	Empirical formula (sample core)
Ar1100	25°C/h→1100°C/4 h(Ar)	25.0	2.04 ± 0.03	2.30	88 ± 1	Si _{1.00} C _{0.62} N _{0.93} O _{0.20}
Ar525	25°C/h→525°C/13 h(Ar) + 1100°C/4 h(Ar)	24.8	2.03 ± 0.02	2.30	88.3 ± 0.8	Si _{1.00} C _{0.66} N _{0.86} O _{0.06}
NH550	25°C/h→550°C/6 h(NH ₃ 10%)	19.5	1.02 ± 0.01	1.35	75.5 ± 0.1	Si _{1.00} C _{0.07} N _{1.30} O _{0.20}
NH800	25°C/h→800°C/4 h(NH ₃ 10%)	22.3	1.68 ± 0.01	2.39	70.3 ± 0.4	Si _{1.00} C _{0.02} N _{1.27} O _{0.12}
NH1000	25°C/h→1000°C/4 h(NH ₃ 10%)	26.9	1.79 ± 0.03	2.48	72 ± 1	Si _{1.00} C _{0.01} N _{1.20} O _{0.13}
NH 1000p	25°C/h→1000°C/4 h(NH ₃ 100%)	28.5	1.80 ± 0.02	2.52	71.4 ± 0.8	Si _{1.00} C _{0.01} N _{0.81} O _{0.14}
NH1100	25°C/h→1100°C/4 h(NH ₃ 10%)	29.3	1.80 ± 0.02	2.52	71.4 ± 0.4	Si _{1.00} C _{0.01} N _{1.20} O _{0.09}

^a Δm %, measured weight loss of the specimen after pyrolysis.

^b ρ , apparent (bulk) density of the specimen determined by the Archimedes method in water (g cm⁻³).

^c ρ_T , skeletal (theoretical) density of the specimen measured by pycnometry in cyclohexane (g cm⁻³).

^d ρ %, relative density of the specimen.

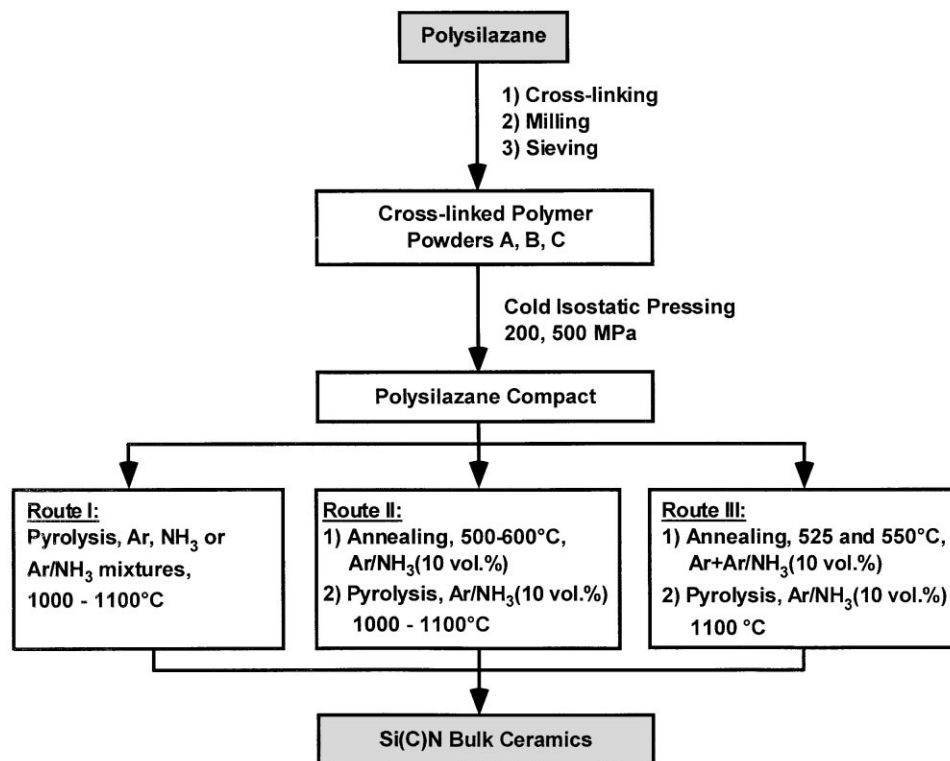


Fig. 2. Flow diagram showing the polysilazane processing and annealing schedules applied for the sample preparation.

Table 3. Heat treatments, carbon contents and empirical formulae of powder B cold-isostatically pressed at 500 MPa and subsequently pyrolysed in Ar/NH₃ (10 vol%) atmosphere with annealing at transient temperatures in Ar/NH₃ (10 vol%) prior to the ceramisation

Sample	Heat treatment	C content (wt%)		Empirical formula (sample core)
		Outer shell	Core	
500NH24	500°C/24 h(NH ₃ 10%) + 1000°C/4 h(NH ₃ 10%)	3.4	5.8	Si _{1.00} C _{0.24} N _{1.20} O _{0.09}
525NH6	525°C/6 h(NH ₃ 10%) + 1100°C/4 h(NH ₃ 10%)	1.1	6.0	Si _{1.00} C _{0.25} N _{1.26} O _{0.08}
525NH9	525°C/9 h(NH ₃ 10%) + 1100°C/4 h(NH ₃ 10%)	1.2	4.0	Si _{1.00} C _{0.17} N _{1.33} O _{0.13}
525NH12	525°C/12 h(NH ₃ 10%) + 1100°C/4 h(NH ₃ 10%)	0.5	0.7	Si _{1.00} C _{0.03} N _{1.27} O _{0.04}
550NH6(200) ^a	550°C/6 h(NH ₃ 10%) + 1100°C/4 h(NH ₃ 10%)	0.8	1.2	Si _{1.00} C _{0.05} N _{1.27} O _{0.20}
550NH6	550°C/6 h(NH ₃ 10%) + 1100°C/4 h(NH ₃ 10%)	1.1	3.0	Si _{1.00} C _{0.13} N _{1.25} O _{0.20}
550NH7.5	550°C/7.5 h(NH ₃ 10%) + 1100°C/4 h(NH ₃ 10%)	0.9	2.5	Si _{1.00} C _{0.10} N _{1.29} O _{0.07}
550NH9	550°C/9 h(NH ₃ 10%) + 1100°C/4 h(NH ₃ 10%)	0.4	0.6	Si _{1.00} C _{0.02} N _{1.27} O _{0.15}
550NH24	550°C/24 h(NH ₃ 10%) + 1000°C/4 h(NH ₃ 10%)	0.4	0.4	Si _{1.00} C _{0.02} N _{1.28} O _{0.12}
600NH24	600°C/24 h(NH ₃ 10%) + 1000°C/4 h(NH ₃ 10%)	4.1	4.1	Si _{1.00} C _{0.19} N _{1.26} O _{0.14}

^aPressed at 200 MPa.

Table 4. Heat treatments, carbon contents and empirical formulae of powder B cold-isostatically pressed at 500 MPa and subsequently pyrolysed in Ar/NH₃ (10 vol%) with annealing at transient temperatures in Ar and in Ar/NH₃ (10 vol%) or Ar/NH₃ (50 vol%) prior to ceramisation

Sample	Heat treatment	C content (wt%)		Empirical formula (sample core)
		Outer shell	Core	
525Ar5NH5	525/5 h(Ar) + 5 h(NH ₃ 10%) + 1100/4 h(NH ₃ 10%)	9.7	9.9	Si _{1.00} C _{0.40} N _{1.08} O _{0.07}
525Ar5NH8	525/5 h(Ar) + 8 h(NH ₃ 10%) + 1100/4 h(NH ₃ 10%)	1.6	6.1	Si _{1.00} C _{0.25} N _{1.21} O _{0.08}
525Ar5NH20	525/5 h(Ar) + 20 h(NH ₃ 10%) + 1100/4 h(NH ₃ 10%)	—	1.9	Si _{1.00} C _{0.08} N _{1.27} O _{0.07}
525Ar5NH8(50)	525/5 h(Ar) + 8 h(NH ₃ 50%) + 1100/4 h(NH ₃ 50%)	1.3	4.7	Si _{1.00} C _{0.20} N _{1.26} O _{0.18}
525Ar15NH8	525/15 h(Ar) + 8 h(NH ₃ 10%) + 1100/4 h(NH ₃ 10%)	4.1	7.1	Si _{1.00} C _{0.29} N _{1.19} O _{0.07}
525Ar15NH12	525/15 h(Ar) + 12 h(NH ₃ 10%) + 1100/4 h(NH ₃ 10%)	0.9	1.4	Si _{1.00} C _{0.06} N _{1.26} O _{0.06}
525Ar5-550NH8	525/5 h(Ar) + 550/8 h(NH ₃ 10%) + 1100/4 h(NH ₃ 10%)	0.7	2.1	Si _{1.00} C _{0.03} N _{1.29} O _{0.05}
550Ar5NH8	550/5 h(Ar) + 8 h(NH ₃ 10%) + 1100/4 h(NH ₃ 10%)	1.2	1.9	Si _{1.00} C _{0.08} N _{1.33} O _{0.07}

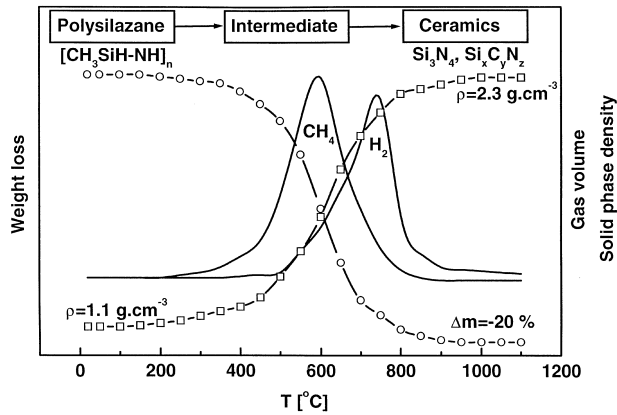


Fig. 3. Schematic of the principal qualitative change in mass and density versus temperature during pyrolysis of poly (hydridomethyl)silazanes.

Si_3N_4 ^{11,12} or $\text{Si}_3\text{N}_{3.4}$ ¹³ were prepared by heat treatment in NH_3 atmosphere. This behaviour indicates, that mixed Ar/ NH_3 furnace atmospheres and suitable heating conditions can yield compositions with precisely tailored carbon contents in the range from 0 to approximately 14 wt%.

In this work, the transient thermal annealing and the final polymer to ceramic conversions were all performed with cold isostatically pressed polysilazane powders. Their crack-free conversion to amorphous silicon carbonitride compacts requires infusible polymers with a defined degree of cross-linking as described by Riedel *et al.*⁴ As depicted in Fig. 2, the fabrication of Si(C)N bulk samples with varying carbon contents involves four steps, namely (i) cross-linking, (ii) pressing, (iii) transient annealing and (iv) pyrolysis. In the following this monolithic processing of the polysilazanes and the final carbon content of the Si(C)N ceramics as influenced by the cross-linking, pressing and pyrolysis is discussed.

3.2 Cross-linking

As shown in Table 1 and in Fig. 2, three types of polysilazane powders A, B and C which can be distinguished by their degree of cross-linking have been prepared for this study:

- Powder A: under-cross-linked
- Powder B: optimally cross-linked
- Powder C: over-cross-linked

The degree of cross-linking obtained after the heat treatment of the poly(hydridomethyl)silazane at 350 or 600°C is characterised by thermo-mechanical analysis (TMA) as shown in Fig. 4. Powder A exhibits extensive melting at $T \geq 280^\circ\text{C}$ indicating the under-cross-linked state while powder B is characterised by a shrinkage between 340 and 600°C caused by partial softening of the polysilazane. It turned out by our studies that the thermal behaviour of the material B is in particular

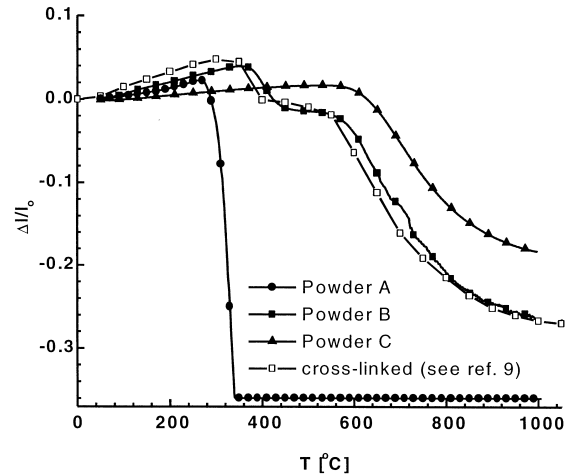


Fig. 4. Thermal mechanical analysis (TMA) of the cross-linked polysilazane powders A, B and C in flowing Ar; heating rate: 300°C/h.

suitable for the monolithic processing of polysilazane powders as found by Riedel *et al.*⁴ and Frieß.¹⁰ Therefore, the degree of cross-linking of powder B is denoted as optimal. In contrast, the characteristic slope of the TMA curve at $T \geq 340^\circ\text{C}$ cannot be measured with powder C and the material is defined as over-cross-linked. The shrinkage at $T \geq 600^\circ\text{C}$ as found for samples B and C is due to structural rearrangements during the ceramisation process. One important consequence of the differently heat-treated powders is that the optimally cross-linked sample shrinks linearly by 27% whereas in the over-cross-linked material the length is reduced only by 19% after pyrolysis at 1000°C.

Figure 5 shows the corresponding results of the thermal gravimetric analysis (TGA) of the cross-linked polysilazane powders B and C. Two gradual weight changes in the temperature intervals between 230 and 420°C and between 470 and 750°C reaching a total weight loss of 22.5% at

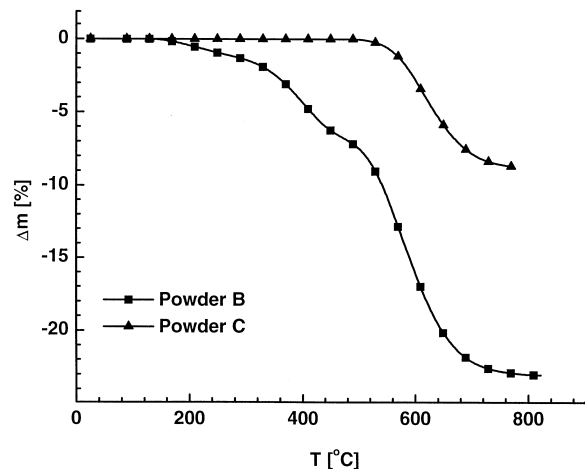


Fig. 5. Thermal gravimetric analysis (TGA) of the cross-linked polysilazane powders B and C in flowing Ar, heating rate: 300°C/h.

800°C are found for powder B while the over-cross-linked polymer C shows no weight change up to 545°C. Polysilazane C reveals only a 7% decrease in weight between 545 and 800°C. These results indicate that the main part of the thermolytic reactions contributing to weight loss and gas evolution during pyrolysis is completed after cross-linking at 600°C.

The chemical composition of powder B is analysed to be $\text{Si}_{1.00}\text{C}_{1.31}\text{N}_{0.91}\text{O}_{0.10}\text{H}_{4.47}$, while cross-linking of the poly(hydridomethyl)silazane at 600°C (sample C) gives $\text{Si}_{1.00}\text{C}_{0.91}\text{N}_{0.85}\text{O}_{0.10}\text{H}_{2.90}$. The analysed carbon content of powder C is lower than that of B, while the nitrogen content remains nearly unchanged in both samples. This result is in agreement with previously published mass spectrometric data¹ which report evolution of CH_4 and H_2 in the temperature range between 400 and 900°C, exclusively.

3.3 Green body consolidation

Cold isostatic pressing of powder B at 200 and 500 MPa gives green compacts with densities of approximately 80 and 90% relative to the skeletal polymer density of 1.22 g cm^{-3} , respectively.¹⁰ The densities of the pressed samples as measured by the Archimedes method are in excellent agreement with the results obtained by mercury pressure porosimetry. It is evident from Fig. 6 that the open porosity as well as the mean pore diameter increase with enhanced degree of cross-linking and with decrease of the applied isostatic pressure. In comparison to polysilazane B, the over cross-linked powder C is comprised of a rigid polysilazane network which cannot be deformed by cold-isostatic pressing. Thus relative densities of approx. 66 and 72% for 200 and 500 MPa were obtained, respectively.

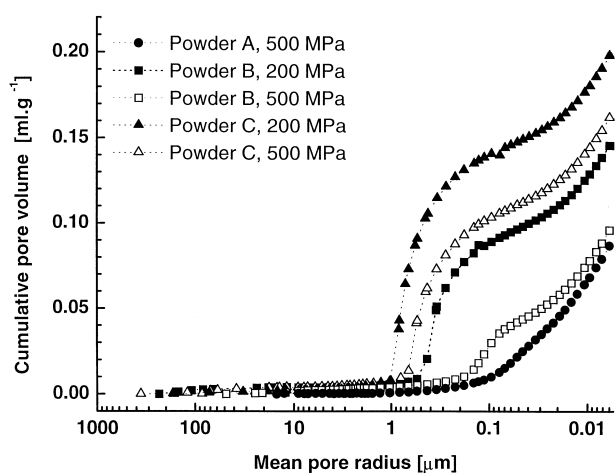


Fig. 6. Pore size distribution measurements (Hg-pressure porosimetry) of cross-linked polysilazane powders B and C cold isostatically pressed at 200 and 500 MPa.

3.4 Transient annealing and pyrolysis

The transient annealing and pyrolysis experiments were all performed with cross-linked and compacted polysilazane B powder. The samples investigated were cold-isostatically pressed at 200 or 500 MPa as indicated in the text.

3.5 Pyrolysis under argon atmosphere

Pyrolysis in argon atmosphere at 1100°C (sample Ar1100 in Table 2) yields black, crack-free and X-ray amorphous Si(C)N ceramics. Shrinkage of the samples during pyrolysis was measured to be $26 \pm 1\%$ in diameter and $24 \pm 3\%$ in sample height. Weight loss was found to be $25 \pm 2\%$ of the original sample weight. The bulk density of the pyrolysed specimens was analysed by the Archimedes method in water to be $2.04 \pm 0.03\text{ g cm}^{-3}$ corresponding to $88 \pm 1\%$ of the theoretical density 2.30 g cm^{-3} determined by pycnometry in cyclohexane. These results are consistent with the value obtained from mercury pressure porosimetry, where an open porosity of 13.1 vol% was found for the pyrolysed specimen.

The carbon content in the pyrolysed specimen Ar1100 was analysed to be 13.2 wt%. The chemical composition can then be expressed as $\text{Si}_{1.00}\text{C}_{0.62}\text{N}_{0.93}\text{O}_{0.20}$. It turned out that an isothermal annealing at a transient temperature in Ar promotes the formation of Si-C bonds. A carbon content of 16.1 wt% with the corresponding empirical formula $\text{Si}_{1.00}\text{C}_{0.66}\text{N}_{0.86}\text{O}_{0.06}$ is obtained in the case a pre-heating of the compacted powder B at 525°C for 13 h in Ar is applied before the final pyrolysis at 1100°C (sample Ar525).

The determined compositions of the pyrolysed specimens Ar1100 and Ar525 are non-stoichiometric in terms of Si_3N_4 and SiC and can be represented by the general formula $\text{Si}_{3+x}\text{C}_x\text{N}_4$. Thus, the samples contain a certain amount of excess carbon (C_y). The reactions of carbon with ammonia at elevated temperatures were studied by several authors.¹⁴⁻¹⁷ It was reported that carbon residues from conventional ceramic greenware can be removed by a reactive heat treatment in NH_3 at $T > 700^\circ\text{C}$ [eqn (1)].



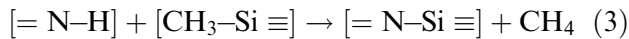
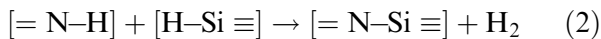
In contrast, the excess carbon in our compacted silicon carbonitride bulk ceramics with open porosities between 30 and 13 vol% cannot be reduced by such a subsequent ammonia treatment. The specimens showed no variation in weight and no change in the carbon content even after 12 h exposure in NH_3 at 1000°C. This finding indicates that after pyrolysis of the polysilazane compacts at 1100°C in inert atmosphere, carbon is completely

embedded in the silicon carbonitride network and is not accessible to form HCN with NH_3 . From our TGA/MS studies concerning the decomposition behaviour of poly(hydridomethyl)silazane to Si(C)N ceramics between room temperature and 1400°C , we can exclude the formation of HCN and NC-CN.^{1,18}

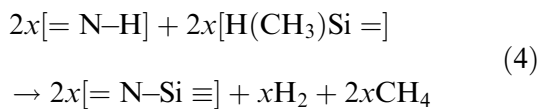
The amount of carbon formed after the final pyrolysis temperature mainly depends on the type of reactions involved in the decomposition process. According to our previous investigations, CH_4 and H_2 are the main gaseous products evolved during the ceramisation of the poly(hydridomethyl)silazane in Ar between 400 and 900°C .¹ Simultaneously, additional Si–C and Si–N bonds are formed during this transformation of polysilazane to Si(C)N ceramics. Therefore, the total amount of outgassing methane determines the remaining carbon content in the pyrolysed Si(C)N material.

Various reactions can be formally assumed to give methane as well as Si–N and Si–C bonds in order to explain the notable difference of the carbon contents found in samples Ar1100 and Ar525.

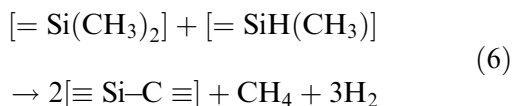
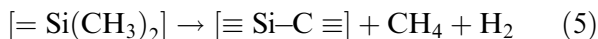
The formation of Si–N bonds can result from reactions (2) and (3):¹⁹



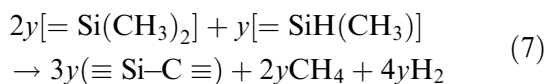
Both reactions forming the Si–N bonds can be summarised by eqn (4):



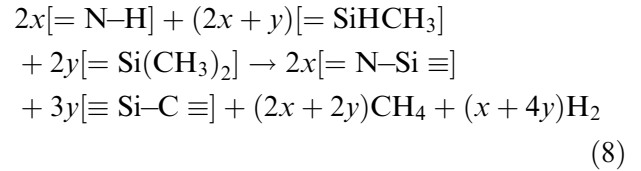
Si–C bonds can be formed by the reactions according to eqns (5) and (6):¹⁹



Reactions eqns (5) and (6) give SiC and can be summarised by eqn (7):



Taking into account reaction eqns (4) and (7), pyrolysis of the poly(hydridomethyl)silazane in argon can be qualitatively estimated by the overall reaction eqn (8):



Bearing in mind the reaction eqn (8) as well as the analytically determined composition of $\text{Si}_{1.00}\text{C}_{1.31}\text{N}_{0.91}(\text{O}_{0.10})\text{H}_{4.47}$ after cross-linking of the polysilazane at 350°C (powder B, Table 1),¹⁰ the composition of the pyrolysed product can then be expressed by the empirical formula $\text{Si}_{1.00}\text{C}_{1.31-2(x+y)}\text{N}_{0.91}\text{H}_{4.47-(10x+16y)}$ where $10x + 16y = 4.47$. The estimation is based on the assumption of ‘ideal’ i.e. oxygen free cross-linked polysilazane. The carbon weight fractions in the pyrolysed product can vary from 10.9 wt% in the case that reaction eqn (4) takes place exclusively ($y=0$, $x=0.447$), up to 18.1 wt% if only reaction eqn (7) is taken into account ($x=0$, $y=0.279$). These considerations are illustrated in Fig. 7. As can be taken from Fig. 7, the reaction parameters are estimated to be $x=0.14$ (31%) for the sample Ar525 while for Ar 1100 the corresponding value is $x=0.31$ (69%). This finding strongly supports that annealing of the poly(hydridomethyl)silazane in Ar at a transient temperature ($500\text{--}550^\circ\text{C}$) prior to pyrolysis favours the proceeding of reactions represented by eqn (7) over that described by eqn (4). Consequently, the outgassing of methane is decreased and, thus, the Si–C bond formation is enhanced by this procedure.

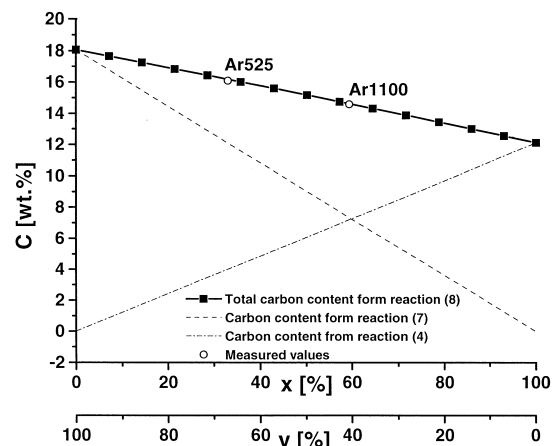


Fig. 7. Weight fractions of carbon in poly(hydridomethyl)silazane powder pyrolysed in Ar as estimated on the basis of the assumed individual reactions given by eqns (4) and (7) and on the overall reaction eqn (8) for $x + y = 0.28 = 100\%$. The experimentally analysed carbon contents of sample Ar1100 and Ar525 are also shown.

3.6 Pyrolysis in reactive atmospheres

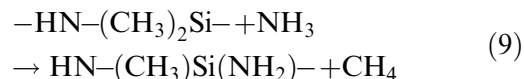
Specimens pyrolysed both in pure NH₃ (NH1000p) and mixtures of Ar/NH₃ up to 550°C (NH550), 800°C (NH800), 1000°C (NH1000) or 1100°C (NH1100) gives white or light tan and X-ray amorphous materials. Weight loss and densities of the samples are listed in Table 2. It is obvious that the weight loss increases with enhanced temperature due to an increased loss of methane and hydrogen during pyrolysis. The degree of ceramisation increases with temperature which is reflected in the skeletal density values of 1.35 and 2.52 g cm⁻³ found for NH550 and NH1000 or NH1100, respectively. The loss of volatile species during the ceramisation was not compensated by any densification mechanism. Therefore, the porosity of the specimens increased with increasing pyrolysis temperature and reached 29 vol% as analysed for the samples NH1000 and NH1100 (Table 2).

The difference in density and porosity of NH1000 and NH1100 is negligible. However, different reactivity towards oxygen and moisture was observed. While NH1100 was inert, the specimens pyrolysed at $T \leq 1000^\circ\text{C}$ changed its colour from white to brown when exposed to air. This finding indicates a reaction of residual Si-H groups present in the sample series ranging from NH550 to NH1000 with moisture or oxygen to form [SiO]_x. The residual Si-H groups can be clearly identified by their characteristic infrared vibration band at 2100–2200 cm⁻¹ as previously reported by Riedel.¹⁸

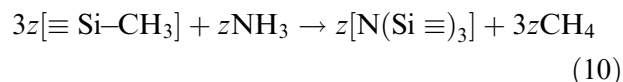
Elemental analysis reveals low carbon contents in all tested specimens decreasing with increasing temperature of isothermal annealing. While in NH550 1.6 wt% C was found, only 0.5 and 0.3 wt% of carbon was detected in samples NH800 and NH1100, respectively. From these results we conclude that the reduction of the amount of carbon is most effective at $T \sim 500\text{--}600^\circ\text{C}$ while the carbon decrease between 800 and 1100°C is only marginal. Therefore, we selected the temperature interval between 500 and 550°C to tune the carbon content in the Si(C)N materials by applying a transient heat treatment in this temperature range prior to pyrolysis at 1000–1100°C (Table 3).

Nearly equal carbon contents are analysed in NH1000, NH1100 (10 vol% NH₃) and NH1000p indicating that the C-reduction is completed after 4 h of isothermal annealing at 1000 or 1100°C and does not depend on the volume ratio of ammonia in the furnace atmosphere. The compositions of the specimens obtained after NH₃ pyrolysis are plotted in the ternary Si-C-N phase diagram shown in Fig. 8(a). It is evident that all the samples decomposed at $T > 800^\circ\text{C}$ under mixed Ar/NH₃ atmospheres contain excess silicon with respect to stoichiometric Si₃N₄ even if the oxygen con-

tamination is considered to form SiO₂. The analysed composition of the sample NH1100 is Si_{1.00}C_{0.01}N_{1.20}O_{0.09} (or Si₃C_{0.03}N_{3.60}O_{0.27}) which formally corresponds to 91 wt% Si₃N₄, 1 wt% SiC, 6 wt% SiO₂ and 2 wt% elemental silicon. In the case of pyrolysis in pure ammonia, the amount of excess silicon is much more pronounced. Treatment of methyl-substituted polysilazanes with NH₃ at elevated temperatures involves the formal substitution of the methyl group attached to the silicon atom by an amino group under release of methane [eqn (9)] as the main reaction contributing to the carbon reduction.^{11,19–21}



Therefore, the bulk compositions of the Si-N materials obtained by pyrolysis of the cross-linked polysilazane Si_{1.0}C_{1.31}N_{0.91}(O_{0.10})H_{4.47}¹⁰ in NH₃ can be qualitatively explained if reaction eqn (10) is taken into account under these conditions:



The Si(C)N composition can be then denoted as Si_{1.0}C_{1.31-3z}N_{0.91+z}H_{4.47-9z}, where $3z = 1.31$ or $0 < z < 0.44$. With $z_{\text{max}} = 0.44$, carbon has been completely evolved in form of methane according to reaction eqn (10) and the formula Si₃N_{4.05}H_{1.53}, with Si/N ratio nearly equal to stoichiometric Si₃N₄ is estimated. Outgassing of the residual hydrogen during thermolysis can proceed e.g. by the formation of gaseous NH₃ resulting in a product with the composition Si₃N_{3.5} which is close to the experimental values Si₃N_{3.53} and Si₃N_{3.43} published by Riedel *et al.*¹³

3.7 Transient annealing in Ar/NH₃ atmospheres prior to pyrolysis

In order to adjust the carbon content more precisely, the pyrolysis experiments were performed with isothermal annealing procedures applied at intermediate temperatures varying from 500 to 600°C. The sample notations, the pyrolysis conditions and the stoichiometries of the pyrolysed Si(C)N products are listed in Tables 3 and 4.

Transient heat treatment in Ar/NH₃ atmosphere at 500, 525 and 550°C yields flawless specimens, while the pellets heat-treated at 600°C contained macro-cracks. All samples were XRD amorphous and scratched common soda-lime glass.

The total linear shrinkage after pyrolysis at 1000 or 1100°C varied between 26 and 27% for both, the sample height and diameter. Mercury pressure porosimetry revealed an open porosity of about

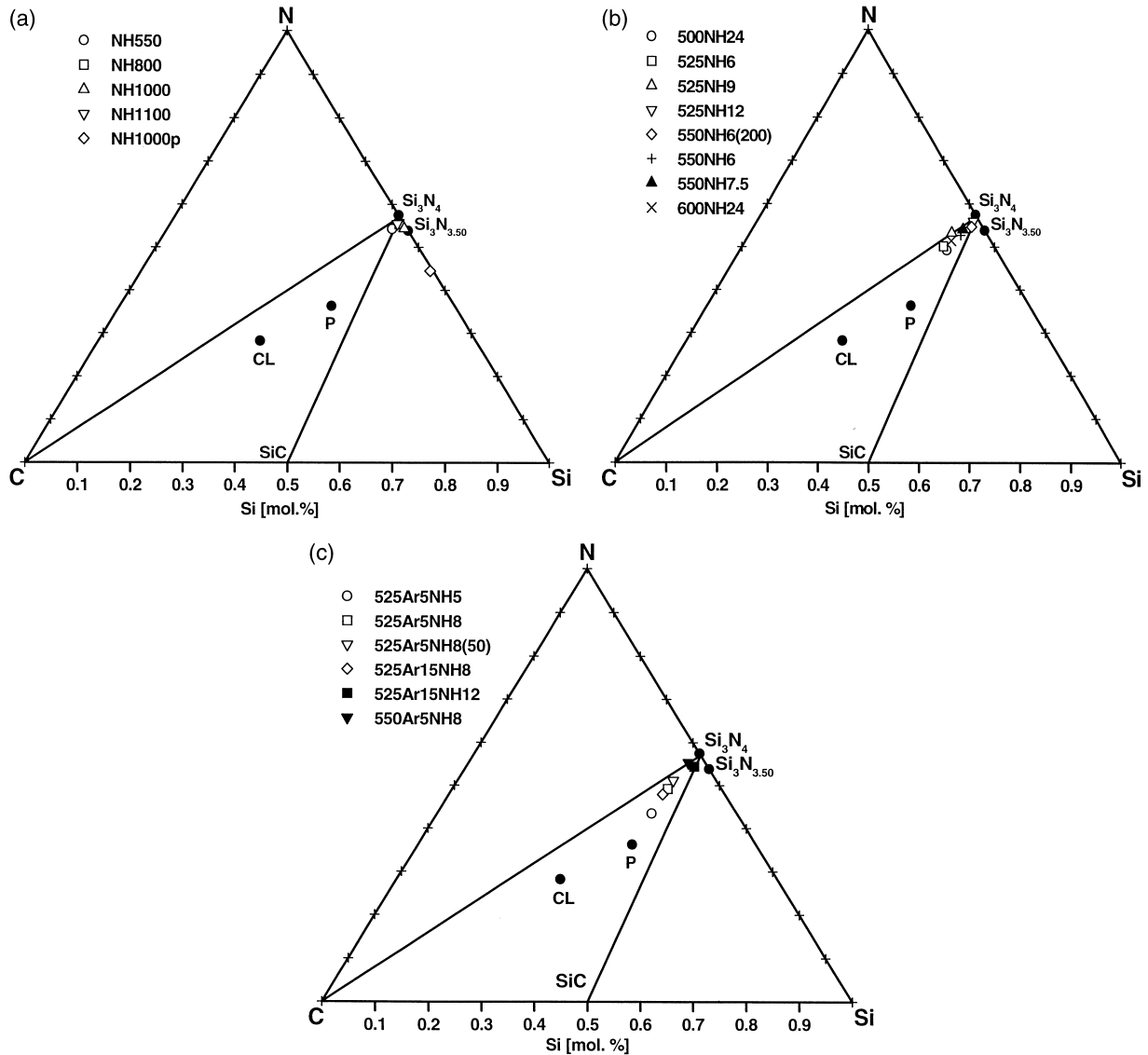


Fig. 8. Schematic illustration of the compositions of the poly(hydridomethyl)silazane derived specimens obtained in reactive atmospheres using different pyrolysis conditions shown in isothermal section of the SiCN phase diagram at $T \leq 1440^\circ\text{C}$. CL and P represent the experimentally determined compositions after cross-linking and after pyrolysis in Ar, respectively. The compositions are given in mol% and oxygen content in the pyrolysed specimens is neglected. (a) Pyrolysis in flowing NH_3 without transient heat treatment. (b) Transient annealing in Ar/ NH_3 atmospheres prior to pyrolysis. (c) Transient heat treatment in Ar and Ar/ NH_3 prior to pyrolysis.

24–26 vol% for all specimens independent of the applied heat treatment schedule.

It is worth to note that the colour of the pyrolysed Si(C)N compacts varied from white to brown. Most of the samples are characterised by a colour gradient changing from brown in the core to white or yellowish in the outer shell. The thickness of the white shell increases with temperature and time of the isothermal transient annealing. The 550NH24 and 600NH24 specimens were homogeneously white all over the specimen volume. Generally, the carbon concentration was measured to be lower in the white shell than in the brown core (Table 3). The compositional difference is increasingly pronounced in the samples with decreasing annealing time at 525 or 550°C (C-gradient: 525NH12 < 525NH9 < 525NH6 and 550NH24 < 550NH9 < 550NH7.5 < 550NH6) and with increas-

ing cold isostatic pressure used for sample preparation. Due to a higher open porosity determined for the sample 550NH6(200) compacted at 200 MPa compared to the specimen 550NH6 pressed at 500 MPa, the C-gradient between the interior matrix and the outer shell in the latter sample is 1.9 wt% while that of the former Si(C)N compact is found to be 0.4 wt%. This result reflects the strong influence of the compacted polysilazane green density on the bulk carbon reduction.

The oxygen contamination in the core did not exceed 4 wt%, while the outer shell contained up to 20 wt% of oxygen due to manipulation of the samples in air. Thus, the formation of amorphous silicon oxynitrides ($\text{Si}_2\text{N}_2\text{O}$) in the outer shell of the specimens and its crystallisation at elevated temperatures have to be considered.

The Si(C)N core materials prepared by transient

annealing in ammonia or mixed NH_3/Ar furnace atmosphere are nitrogen-rich and contain 33 to 38 wt% nitrogen while the level of carbon is relatively low and increases from 0.4 to 6 wt% with decreased temperature and time of transient heat treatment [Table 3, Fig. 8(b)]. Comparing the samples 550NH24 and 600NH24 reveals that at $T \geq 550^\circ\text{C}$ as the intermediate annealing temperature, (i) the difference in the carbon content between core and shell is aligned and (ii) the core carbon concentration increases with exceeding temperature. Consequently, the most effective transient annealing for the carbon reduction ammonia atmospheres is found to be in the temperature range between 525 and 550°C .

These results also suggest that pyrolytic reactions of the type given by eqn (9) dominate the behaviour in NH_3 and mixed Ar/NH_3 reactive atmospheres with and without transient annealing, while contributions related to reactions as represented by eqns (4) and (7) are negligible.

3.8 Transient heat treatment in Ar and Ar/NH_3 prior to pyrolysis

As discussed before, heat treatment in argon at a transient temperature promotes the Si–C bond formation during thermolysis and increases the carbon concentration in the poly(hydridomethyl)-silazane-derived silicon carbonitride. Therefore, an additional period of isothermal annealing in argon was included into the pyrolysis schedule before modifying the carbon level by reactive heat treatment in NH_3 . The pyrolysis conditions and chemical compositions of the pyrolysed Si(C)N materials are listed in Table 4. The compositions as located in the Si–C–N ternary phase diagram are also shown in Fig. 8(c).

Accordingly, specimens pre-treated in argon reveal higher carbon contents than that pre-heated in ammonia at $500\text{--}550^\circ\text{C}$. Thus, the sample 525Ar5NH5 contains 9.9 wt% C in the core and 9.7 wt% of carbon in the shell. The specimen 525Ar5NH20 heated for 20 h in Ar/NH_3 (10%) at 525°C contained 1.9 wt% of core carbon compared to 0.7 wt% in 525NH12.

Prolonged transient annealing in Ar increased the level of bonded carbon and hence decreased the influence of subsequent ammonia treatment. The increase of the carbon concentration in the specimens pre-heated in Ar at 525°C for 5 h (sample 525Ar5NH8, 6.1 wt% in the core and 1.6 wt% in the shell) and 15 h (sample 525Ar15NH8, 7.1 wt% and 4.1 wt% in the core and shell respectively) and subsequently pyrolysed in Ar/NH_3 (10%) is evident (see also Table 4).

This finding again points out that pre-treating the polysilazane samples in argon at about $500\text{--}550^\circ\text{C}$ results in an enhanced formation of additional Si–

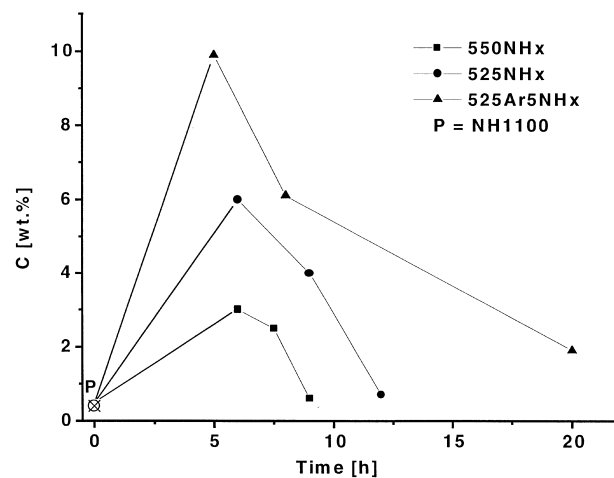


Fig. 9. Change of carbon contents in pyrolysed Si(C)N specimens versus isothermal transient annealing time x at 525 and 550°C under different atmospheres. For sample notation see Table 3 and Table 4. Sample P represents the carbon fraction of the polysilazane heat-treated to 1100°C under NH_3 atmosphere without any intermediate annealing (see Table 2).

C bonds and increased carbon contents. The compositions of the argon pre-treated specimens are shifted closer to the SiC– Si_3N_4 tie line compared to the samples annealed in ammonia prior to pyrolysis [Fig. 8(b)]. However, only the specimen 525Ar15NH12 containing 1.4 wt% C—which is equivalent to 5 wt% of SiC—after its decomposition at 1100°C is in the range of the compositions with the general $\text{Si}_{3+x}\text{C}_x\text{N}_4$ stoichiometry which are located directly on the tie line between SiC and Si_3N_4 [Fig. 8(c)]. For this particular sample with $x=0.19$, the high temperature stability in terms of decomposition is expected to be enhanced at $T > 1440^\circ\text{C}$ compared to Si(C)N materials with the $\text{Si}_{3+x}\text{C}_{x+y}\text{N}_4$ stoichiometry.

In Fig. 9, the influence of isothermal transient annealing on the final carbon fraction in the Si(C)N ceramics listed in Tables 3 and 4 is illustrated. It is evident that the carbon content increases by applying transient annealing periods between 525 and 550°C in Ar and NH_3 as compared to a sample directly heated to 1100°C .

It is noteworthy to mention that the carbon content of compacted and over-cross-linked powders C cannot be effectively influenced by transient heat treatments at $500\text{--}600^\circ\text{C}$. The applied high cross-linking temperature of 600°C leads to almost unreactive polysilazane with a fixed carbon amount of about 7 wt%.

4 Conclusions

It was shown in the present work that the carbon content in bulk amorphous Si(C)N ceramics prepared by pyrolysis of cross-linked and compacted poly(hydridomethyl)silazane powders can be adju-

ted *in-situ* from 0.3 up to 16.2 wt%. To prepare crack-free Si(C)N bulk ceramics with different carbon contents, heat treatments of cold isostatically pressed polymer powders in inert (Ar) or reactive (NH₃ or Ar/NH₃) gases were performed. It turned out that time and temperature of transient annealing periods between 500 and 600°C prior to pyrolysis at 1000 or 1100°C as well as the ammonia volume ratio in the furnace atmosphere significantly influence the final carbon contents of the Si(C)N ceramics. The results obtained can be summarised as follows:

- Pyrolysis of bulk specimens in reactive ammonia atmosphere up to 1100°C results in practically carbon-free specimens (0.3 wt% C).
- Carbon content adjustment is most effective between 500 and 550°C as the transient temperature treatment. Controlled outgassing of the volatile reaction products, mainly CH₄ and H₂, provides crack-free Si(C)N samples. Treatment at higher transient temperature ($T > 550^\circ\text{C}$) results in cracked specimens due to rapid gas evolution during pyrolysis.
- Increased transient temperature and a higher ammonia content in the furnace atmosphere promotes the carbon reduction.
- Additional pre-treatment at 525 and 550°C in Ar before annealing of the samples in ammonia promotes the formation of Si–C bonds and gives higher carbon contents after pyrolysis.
- Our experiments proved that pyrolysis of poly(-hydridomethyl)silazane in argon cannot yield Si(C)N ceramics with compositions located on the tie line between SiC and Si₃N₄. However, for the pyrolysis in reactive NH₃ atmospheres, silicon carbonitride ceramics with a tie-line composition corresponding to 5 wt% SiC is prepared by transient annealing of the polysilazane in the temperature range between 500 and 550°C in mixed Ar/NH₃ atmosphere and subsequent pyrolysis at 1000–1100°C.

Acknowledgements

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