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Silicon carbonitride ceramics derived from polysilazanes Part I. Investigation of compositional and structural properties

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Abstract

In this paper we report on the compositional and structural properties of ceramics in the Si–C–N system. The amorphous material synthesised by thermally induced ceramisation of an organo-substituted polysilazane crystallises at temperatures exceeding 1450°C in nitrogen atmosphere. Chemical composition, solid state structure, microstructure as well as the crystallisation behaviour depend on: (i) the synthesis conditions; (ii) the pyrolysis atmosphere; and (iii) the time and temperature of a final heat treatment. The chemical composition was determined by chemical bulk analysis together with ^{15}N-method and electron energy-loss spectroscopy (EELS). Reaction products formed during the heat treatment were analysed in-situ by thermal gravimetric analysis coupled with mass spectrometry. The hybridisation of carbon in the solid reaction product was determined by X-ray absorption near-edge structure (XANES). The resulting amorphous microstructure was investigated by electron microscopy (HRTEM), while the crystalline phases were analysed by X-ray diffraction (XRD).

Keywords: Electron microscopy; Microstructure-final; Polysilazane; Precursors-organic; Si–C–N; X-ray methods

1. Introduction

The fabrication of carbide and nitride based materials by the polymer-to-ceramic conversion route has attained increasing interest in particular for the preparation of dense and porous ceramics and ceramic composites, fibres and coatings.[1–3] One substantial benefit of the precursor-derived ceramics is their potentially simple processing to complex shaped forms by extrusion and injection moulding of polymeric ceramic precursors as well as by the machining of polymeric parts. Subsequent pyrolysis provides the ceramic component. The volume shrinkage associated with the polymer-to-ceramic transformation can be reduced and adjusted by the addition of reactive or non-reactive fillers.[4] Following this route, novel thermomechanically stable ceramic materials can be synthesised which are not accessible by conventional methods. Accordingly, polymer-derived, non-stoichiometric and amorphous silicon carbonitride with the composition $Si_{1.7}C_{1.0}N_{1.5}$ exhibits extraordinary oxidation and creep resistance.[5–7] Considering the silicon carbonitride as a glass, the glass transformation point T_g is far beyond that of quartz and other oxidic glasses.[6,7] The amorphous silicon carbonitride considered in our study is thermally stable with respect to crystallisation and/or decomposition up to 1400°C in 0.1 MPa nitrogen or argon gas and up to 1600°C in air.[5]

Depending on the organosilicon precursor, the composition of the silicon carbonitride formed after thermolysis at about 1100°C under Ar or N_2 can vary from carbon-rich to nitrogen-rich SiCN.[1,8,9] While most of the existing literature has reported on former compositions which give SiC and carbon after crystallisation,[10–12] here we report on a nitrogen-rich silicon carbonitride derived from poly(hydridomethyl)silazane which partitions to Si_3N_4/SiC micro/nano-composites at $T > 1450$°C. Our objective in this study is to analyse the electronic properties of this kind of material in relation to its microstructure which in turn is a function of the annealing procedure. Therefore, we have organised the discussion of our investigation as follows: Part I, we

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focus on compositional and microstructural changes of this particular nitrogen-rich silicon carbonitride heat treated at different temperatures between 1000 and 1700°C. In Part II, we present the electrical properties (dc- and ac-conductivity, permittivity and thermopower) of $Si_{1.7}C_{1.0}N_{1.5}$ subjected to different annealing procedures and discuss the respective conducting mechanisms correlated with the microstructural changes.[13]

2. Experimental procedure

Poly(hydridomethyl)silazane (NCP 200, Nichimen Corp., Japan), was used as the starting organosilicon polymer. First, the preceramic polymer was cross-linked at about 350°C in Ar resulting in an infusible polymer. After milling and sieving, cold isostatic pressing of the polysilazane powder at 500 MPa was applied to produce a compact which was then pyrolysed at 1000°C in Ar. This procedure gave an amorphous ceramic with the chemical composition $Si_{1.7}C_{1.0}N_{1.5}$ after outgassing of CH_4 and H_2. Details of the monolithic processing of cross-linked poly(hydridomethyl)silazane to silicon carbonitride ceramics were reported in Refs. 14 and 15

After the thermally induced ceramisation, the amorphous ceramics were heat-treated in a graphite furnace under nitrogen atmosphere (flow rate 5 l/h). The ramping rate was 10°C/min between room temperature and 1000°C followed by 2°C/min up to the final annealing temperature T_a. The holding time t_a ranges from 5 to 50 h.

The bulk density of the ceramics described above was measured both by the Archimedes method and geometrically. Additionally, bulk and solid state density as well as open porosity were determined by a mercury pressure porosimetry with a poresizer 9320, Micromeritics.

The chemical composition was evaluated by hot gas extraction (analyser EC 12 for carbon and TC 436 for nitrogen and oxygen, Leco Corporation, USA). The hydrogen content was determined using the ^{15}N-method performed at the University of Frankfurt, Germany. Hydrogen reacts with incident nitrogen ions which have an energy exceeding 6.385 MeV forming carbon, α- and γ-radiation. The detected number of γ-quantums can be used to evaluate the hydrogen content.[16,17]

Mass loss and outgassing species during tempering were monitored by using a simultaneous thermal analysis device (Netzsch STA 429) coupled with a mass spectrometer (Balzers QMG 420).

The hybridisation of the element carbon in the amorphous materials was investigated by X-ray absorption near-edge structure (XANES) measurements performed at the Bonn electron stretcher and accelerator (ELSA), Germany. The C_K-spectra were obtained using a high-energy toroidal grating monochromator in the electron yield mode. The energy of the incident radiation was in the range between 270 and 330 meV with a resolution of about 10^{-3}.

The microstructure of the Si–C–N materials was characterised employing a Jeol 4000 EX electron transmission microscope, operating at 400 keV. The point-to-point resolution of this instrument was 0.18 nm. In addition, a Philips CM20FEG (field emission gun) microscope, operating at 200 keV giving a point-to-point resolution of 0.24 nm, was used with an electron energy-loss spectrometer (PEELS, Gatan 666) attached to it. Under optimised working conditions, an energy resolution of 0.80 eV was achieved. EELS data acquisition were performed with an energy dispersion of 0.3 eV. Transmission electron microscopy (TEM)/foil preparation followed standard techniques like cutting, grinding, dimpling, and Ar-ion thinning to perforation. Light carbon coating allowed to minimize electrostatic charging during TEM observation.

The crystalline phases were investigated, apart from electron diffraction techniques involving selected area diffraction (SAD) and microdiffraction, using X-ray powder diffraction on a powder diffractometer (Siemens D 5000, Germany).

The detection of sp^2-hybridised carbon containing phases was performed by Raman spectroscopy. The spectra were recorded at room temperature using a RFA 106 accessory (Bruker, Germany). The laser excitation was supplied by a Nd:YAG laser, operating with a power of about 100 mW.

3. Results and discussion

In contrast to polyvinylsilazane or polycarbosilazane, the thermal decomposition of poly (hydridomethyl)silazane results in the formation of silicon carbonitride with relatively low carbon contents (see Table 1). It has been shown in a series of studies that besides the molecular structure of the preceramic compound, the Si–C–N ratio influences the partitioning and crystallisation behaviour of the materials (see for example, see refs. [3,8,10,11]).

Pyrolysis of poly(hydridomethyl)silazane gives a silicon carbonitride with a nitrogen and silicon rich composition ($Si_{1.7}C_{1.0}N_{1.5}$) which does not change up to 1450°C and which crystallises to Si_3N_4/SiC composites at higher temperatures. Silicon carbonitrides with higher carbon contents provide SiC/C mixtures upon crystallisation.[10]

In the following, we discuss the thermal behaviour of poly(hydridomethyl)silazane-derived silicon carbonitride bulk samples in terms of compositional and microstructural variations at temperatures between 1000 and 1700°C.

Table 1
Chemical composition of Si–C–N-ceramics derived from poly(hydridomethyl)silazane

Sample	Chemical composition [wt%]				
	Si	C	N	O	H
Preceramic polymer					
NCP 200[a]	43	28	22	n.d.[c]	8.4
After cross-linking at 350°C/4h	45	26	21	n.d.	7.2
Pyrolysed sample					
1000°C/4 h/Ar	58[b]	13	25	3.4	0.3
Heat treatment in N_2					
1450°C/50 h	58[b]	13	28	1.6	n.d.
1500°C/10 h	58	14	25	2.4	n.d.
1500°C/50 h	61[b]	19	15	4.1	n.d.
1700°C/5 h	64[b]	17	17	1.5	n.d.

[a] Calculated from $[(CH_3)_2SiNH]_{0.5}(CH_3SiHNH)_{0.25}(CH_3SiN)_{0.25}$. The formal composition of poly(hydridomethyl)silazane NCP200 was provided by Chisso Crop., Tokyo, Japan.

[b] Calculated by using $m_{Si} = 100 - \sum_i m_i(\%)$ (m_i = weight content of C, N, O).

[c] n.d., not determined.

3.1. *Density, mass loss, shrinkage and porosity*

In particular, the change in density and porosity, the mass loss and shrinkage during subsequent heat treatment of the as-synthesised silicon carbonitride in 0.1 MPa N_2 were analysed. Nitrogen was used as the annealing gas to hamper the solid state reaction of silicon nitride with carbon to form SiC and N_2 which becomes relevant at temperatures above 1450°C [reaction equation (1)].[18] Moreover, nitrogen suppresses the self-decomposition of silicon nitride formed from the amorphous SiCN-phase [reaction equation (2)].

$$Si_3N_4 + 3C \Longleftrightarrow 3SiC + 2N_2 \tag{1}$$

$$Si_3N_4 \Longleftrightarrow 3Si + 2N_2 \tag{2}$$

Densification of the Si–C–N ceramic was measured, which depends on the time and the temperature of the annealing procedure (Figs. 1 and 2). Three different temperature regions with a distinct shrinkage behaviour can be identified. At temperatures between 1000 and 1300°C (region I) the increase of the bulk density is about 0.1 g/cm^3 accompanied with a decrease of the open porosity. The mass loss is determined to be 1% and is attributed to the loss of residual hydrogen and the formation of CO and SiO (see Sections 3.2 and 3.3). The linear shrinkage caused by the densification and the mass loss is up to 4%. However, the solid state density in this temperature region is nearly constant and is analysed to 2.3 g/cm^3.

Between 1300 and 1500°C (region II) the bulk density increases due to the formation of Si_3N_4 and SiC, which is proved by both TEM and X-ray diffraction (XRD) (Sections 3.5 and 3.6). The composition of the pyrolysed product is located beyond the SiC–Si_3N_4 tie line in the ternary Si–C–N phase diagram. Consequently, the high-temperature decomposition of the amorphous Si–C–N material is accompanied by the evolution of nitrogen resulting in a pronounced mass loss of about 14% and a higher linear shrinkage as compared to temperature region I. With the partial decomposition of the amorphous material, which typically initiates local crystallisation, the solid state density is increased up to 2.7 g/cm^3. In contrast to region I the densification process depends on the holding time at the respective temperature (10 or 50 h).

At temperatures exceeding 1500°C (region III) the bulk density and the linear shrinkage are lower than that in region II. This is in accordance with the formation of nitrogen during the heat treatment, which affects

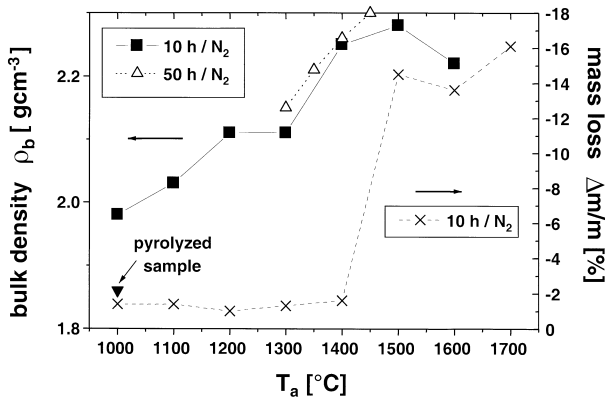


Fig. 1. Bulk density and mass loss of compacted poly (hydridomethyl) silazane-derived silicon carbonitride ceramics depending on the subsequent annealing temperature in 0.1 MPa N_2.

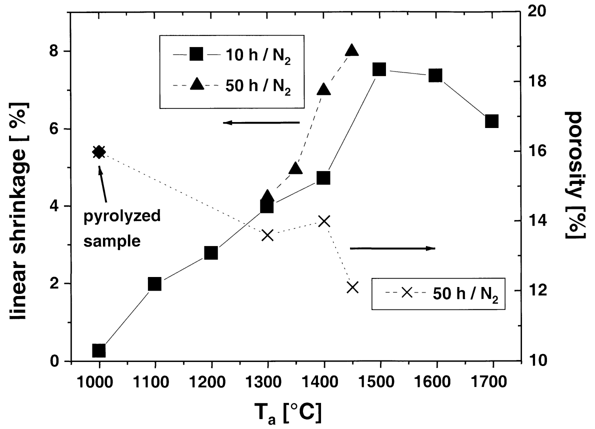


Fig. 2. Linear shrinkage and open porosity of compacted poly-(hydridomethyl)-silazane-derived silicon carbonitride ceramic depending on the subsequent annealing temperature in 0.1 MPa N_2. After annealing for 5 h at 1700°C, an open porosity of 40 vol% was analysed (value not shown in graph).

the porosity of the material. The open porosity at 1700°C can exceed 40% depending on the heating rate. Besides the decomposition of the amorphous material, silicon nitride and free carbon (see Sections 3.4 and 3.7), produced by partitioning of the Si–C–N phase, react to form silicon carbide and nitrogen according to reaction equation (1).

3.2. Chemical composition

In Table 1 the chemical compositions of the Si–C–N ceramics depending on the synthesis and annealing conditions are listed. The outgassing of methane and hydrogen during cross-linking and pyrolysis in Ar results in a decrease of the carbon and hydrogen content while the silicon content is increased and the nitrogen content remains nearly constant.

After isothermal annealing at 1450°C for 50 h respectively 1500°C for 10 h, the Si–C–N composition is nearly unchanged compared to that obtained after pyrolysis at 1000°C. However, a significant mass loss up to 14% is detected indicating that besides nitrogen also CO and SiO are evolved which is proved by in-situ mass spectrometry (see Section 3.3). The amount of nitrogen decreases from about 25 wt% to 15 wt% after a heat treatment at 1500°C for 50 h or at higher temperatures, while the silicon and carbon contents are increased. Consequently, nitrogen is the main gas species which is formed at $T \geqslant 1500$°C.

Moreover, residual hydrogen can be found in the resulting silicon carbonitride after the thermally induced ceramisation. Quantification of the hydrogen content was performed by the ^{15}N-method.[16,17] Accordingly, hydrogen decreases with increasing temperature of the final heat treatment. Fig. 3 shows the rate of γ-quants, which were generated during the incidence of ^{15}N-ions, depending on the depth. The hydrogen content c_H is derived according to the following equations:

The rate between matrix atoms and hydrogen atoms can be described by Eq. (3) which leads to c_H [at%] according to Eq. (4).

$$X = \frac{N_H}{N_{Matr.}} = \frac{N_{\gamma,SiCN}\cdot S_{Matr.}}{N_{\gamma,NH_4Cl}\cdot S_{NH_4Cl} - N_{\gamma,SiCN}\cdot S_H} \qquad (3)$$

with:

N_H	number of hydrogen atoms
$N_{Matr\cdot}$	number of the matrix atoms
$N\gamma,_{SiCN}$	number of γ-quants with Si–C–N target
$N\gamma,_{NH_4Cl}$	number of γ-quants with reference target (NH_4Cl)
S_{Matr}	stopping power of the matrix atoms
S_H	Stopping power of hydrogen
S_{NH_4Cl}	stopping power of NH_4Cl (reference target)

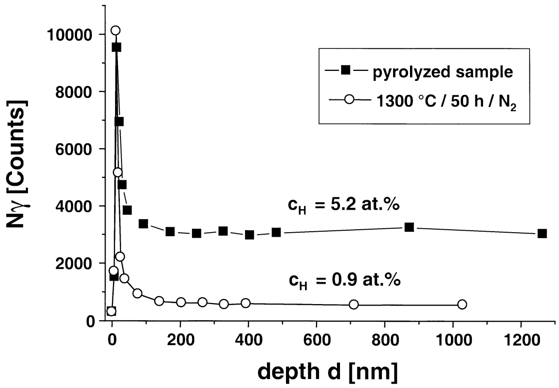


Fig. 3. Hydrogen depth profile of amorphous Si–C–N ceramics after pyrolysis and after 50 h annealing at 1300°C in N_2 as analysed by the ^{15}N-method.

$$c_H = \frac{X}{1+X} \qquad (4)$$

The depth d depends on the energy of the incident nitrogen ions and can be calculated using Eq. (5) with the resonance energy, E_r, of the nuclear reaction being 6.385 MeV:

$$d = (E - E_r)/S_{Matr.} \qquad (5)$$

It is evident from the ^{15}N-measurements that the Si–C–N material contains about 5 at% residual hydrogen after pyrolysis at 1000°C in Ar. The hydrogen content decreases below 1 at% after a heat treatment at 1300°C.

The oxygen contamination of the synthesised and annealed products are analysed to 1.5 up to 4.1 wt% and correlates with that described in the literature for other silicon carbonitrides with different stoichiometries[10,11]. The source for oxygen is caused by the starting commercial precursor NCP200 on the one hand and by the manipulation of the samples in air after pyrolysis and annealing on the other hand.

According to the analytical data, the following formal composition can be derived for the material obtained at 1450°C (see Table 1) by assigning all O and N to SiO_2 and Si_3N_4, respectively, while carbon is then correlated to the remaining amount of silicon atoms: $1\ Si_3N_4 + 1\ SiC + 0.8\ C + 0.1\ SiO_2$. The "free" carbon can either react with silicon nitride to form nitrogen and silicon carbide [see reaction Eq. (1)] or can form gaseous SiO/CO by its reaction with silica at higher temperatures. Therefore, according to the chemical analysis given in Table 1, the composition changes to $4\ SiC + 1\ Si_3N_4 + 0.3\ C + 0.15\ SiO_2$ after proceeding crystallisation at 1700°C. From the analytical point of view it is obvious that a significant amount of silicon nitride is formed from nitrogen-rich poly (hydridomethyl) silazane. In contrast, vinyl substituted polysilazanes and polycarbosilazanes give nitrogen free SiC/C mixtures after partitioning and crystallisation of the amorphous intermediate silicon carbonitride phase.[10,19,20]

3.3. Simultaneous thermal analysis coupled with mass spectrometry

In order to obtain more detailed information about the temperature dependence of the mass loss and the formation of gaseous decomposition products, the stability of the Si–C–N ceramic was studied by simultaneous thermal analysis together with mass spectrometry. Having the same mass, the gases N_2 and CO cannot be distinguished by mass spectrometry. Therefore, mass peaks with $m/e = 14$ and 44 corresponding to N and SiO, respectively were detected. Fig. 4 shows the ion current associated with the masses $m/e = 2$ (H_2), $m/e = 14$ (N) and $m/e = 44$ (SiO) measured between 1300 and 1550°C and during the subsequent isothermal hold at 1550°C. Accordingly, with increasing temperature and holding time the amount of outgassing H_2 and SiO decreases while the amount of nitrogen is increased. Consequently, the nitrogen content of the Si–C–N ceramic decreases with growing temperature and annealing time. Silicon monoxide (SiO) is formed due to the oxygen contamination of the silicon carbonitride (see Table 1). The outgassing of nitrogen is the main reason for the high mass loss detected at temperatures exceeding 1500°C.

3.4. XANES-spectroscopy

Fig. 5 shows the XANES spectra at the C_K-edge of the Si–C–N ceramic after pyrolysis and different annealing temperatures. Graphite and SiC with sp^2- and sp^3-hybridised carbon atoms, respectively, were used as standards. The detected spectra show the following characteristic features:

- At an energy of 285 eV, the peak is attributed to a π^*-resonance caused by C=C bonds.[21] This resonance clearly detected in graphite, is not found in SiC. In silicon carbonitride the height of the π^*-resonance increases with growing temperature which points out the increasing ratio of sp^2/sp^3-hybridisation of the carbon atoms in the amorphous ceramics.
- At 288 eV, a σ^*-resonance characteristic for C–H bonds is found. This peak decreases with increasing temperature of heat treatment. This finding is consistent with the decreasing hydrogen content of the samples with increasing annealing temperature T_a (compare Fig. 3).

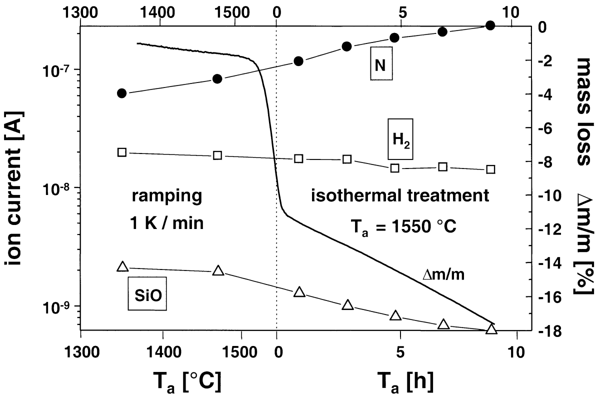


Fig. 4. High-temperature thermal gravimetric analysis coupled with simultaneous mass spectroscopy of poly(hydridomethyl)silazane-derived silicon carbonitride in 0.1 MPa Ar. The graph shows the mass loss Δm/m as well as the ion current of the masses $m/e = 2$ (H_2), 14 (N) and 44 (SiO) detected in the temperature range between 1300 and 1550°C and during isothermal hold at 1550°C for 10 h.

The correlation between the sp^2-hybridisation of carbon and the hydrogen content of the material was experimentally[22] and theoretically[23,24] found for amorphous

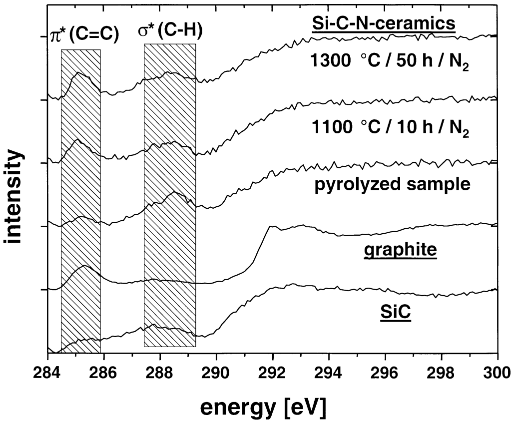


Fig. 5. X-ray absorption near-edge structure (XANES) $C_{K\text{-edge}}$ absorption spectra of Si–C–N ceramics depending on the annealing temperature T_a. Graphite and SiC were used as reference.

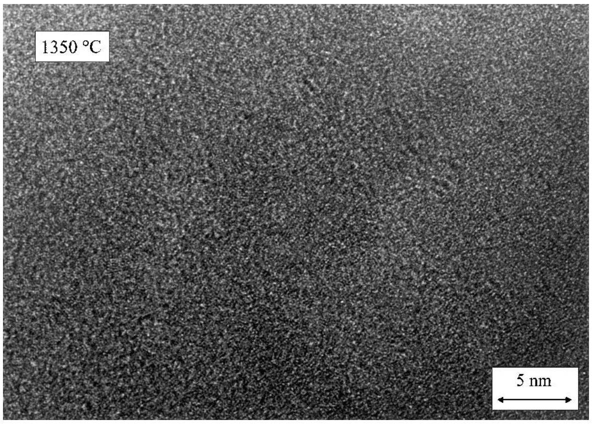


Fig. 6. Electron microscopy (HRTEM) image of Si–C–N ceramic annealed at 1350°C for 50 h in nitrogen.

carbon. It has been shown that the sp^2-fraction of carbon can be reduced from 90 to 30% by hydrogenation. Silicon carbide was reported to reveal a similar behaviour.[25]

3.5. High-resolution TEM

Poly(hydridomethyl)silazane-derived Si–C–N ceramics reveal a pronounced increase of the electrical conductivity after annealing at temperatures exceeding 1300°C. Therefore, a detailed study of the ceramic microstructure development between 1300 and 1500°C was performed. High-resolution TEM imaging revealed a significant change of the microstructure, which is due to both phase partitioning and local nucleation. At 1350°C, heat treatment in nitrogen leads to the formation of micron-sized α-Si_3N_4 crystallites. However, this particular crystallisation of α-Si_3N_4 was only observed in some locally inhomogeneous regions of the sample. The main part of the ceramic remains amorphous, as shown in the HRTEM micrograph of Fig. 6, revealing a homogeneous phase contrast typical for amorphous structures. Samples heat treated in nitrogen at 1450°C for 50 h contained nanocrystalline particles being between 2 and 5 nm in diameter (Fig. 7). The corresponding diffraction patterns also indicate distinct differences between the two samples. When annealing at 1350°C, the diffraction pattern only showed a diffuse ring pattern of elastically scattered electrons, being characteristic for structures of short-range order. However, annealing at 1450°C resulted in the nucleation of nm-sized crystallites and, as a consequence, in the presence of distinct diffraction rings in the SAD pattern (compare Fig. 8). The fact that diffraction rings rather than diffraction spots are seen corresponds to the polycrystallinity of the material on the nm-scale. Using Eq. (6),

$$d = \lambda \cdot L / R \qquad (6)$$

with λ being the electron wave length, d the distance of the interatomic spacing, L representing the camera length employed, and R the measured radii of the respective diffraction rings, gave the corresponding d-values and in turn identified the nucleation of nm-sized β-SiC within the amorphous matrix (compare Table 2 and Fig. 7). According to TEM observations, the amount of the β-SiC volume fraction is estimated to be 16%, indicating the possibility to form a SiC-percolation path. This result coincides with the experimentally determined enhanced electrical conductivity of the annealed silicon carbonitrides.[13]

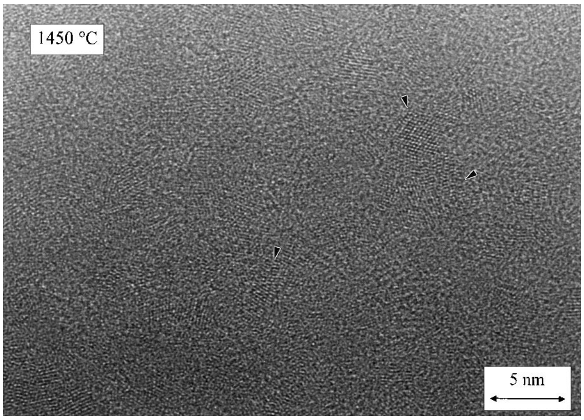


Fig. 7. Electron microscopy (HRTEM) image of Si–C–N ceramic annealed at 1450°C for 50 h in nitrogen. Arrows indicate SiC nanoparticles.

In addition, the amorphous Si–C–N phase undergoes a structural and compositional development during heat

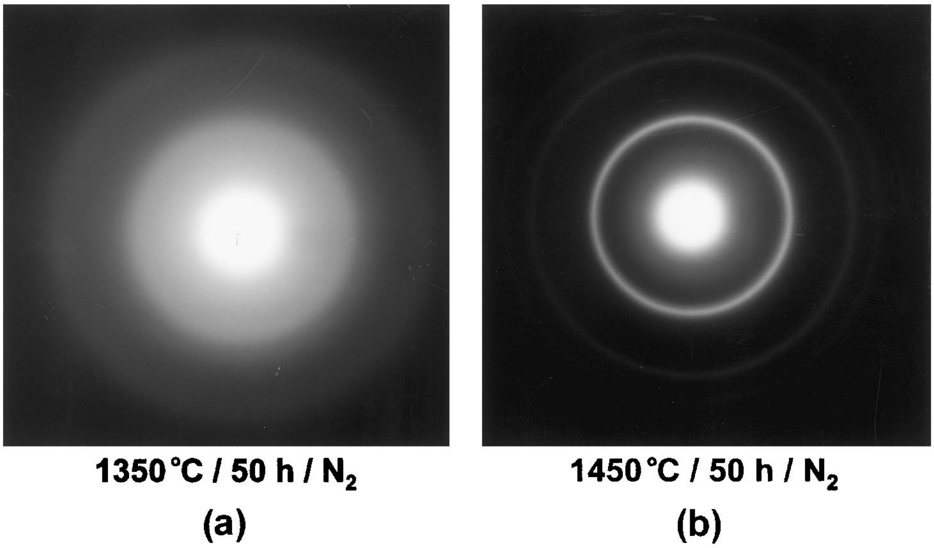


Fig. 8. Electron diffraction pattern (SAED) of Si–C–N ceramic: (a) annealed at 1350°C; and (b) 1450°C for 50 h in nitrogen.

treatment, as proved by EELS analysis given in Fig. 9. Whereas the Si–C–N ceramic annealed at 1350°C shows a homogeneous amorphous microstructure and reveals a N_K-edge as well as a π*-pre-peak of the C_K-edge at 284 eV, these characteristic features are no longer seen upon annealing at 1450°C. This result points out that the volume fraction of nitrogen, as well as the amount of sp^2-hybridised carbon atoms have decreased changing the overall composition of the material to SiC. However, it has to be emphasised that annealing at higher temperatures in fact initiates local crystallisation of SiC and Si_3N_4. Therefore, this material is considered to reveal a more inhomogeneous microstructure which reflects local phase partitioning.

Taking into account the mass loss, chemical composition, and TEM observations, the respective volume fractions of the different phases formed upon Si–C–N pyrolysis at 1000°C and after subsequent annealing at 1450°C can be estimated, as summarized in Table 3.

3.6. *XRD*

The crystalline phases were identified by X-ray powder diffraction (Fig. 10). The diffraction pattern clearly exhibits the presence of α-SiC (6H) and α-Si_3N_4 in the samples annealed above 1500°C. However, below 1500°C the crystalline fraction is rather small. The weak intensities can be also associated with the small grain size of the SiC particles (see Section 3.4) and the detection limit of 5 to 10 vol%.

Above 1600°C, the silicon nitride reflections decrease whereas that of silicon carbide increase, which is due to the proceeding crystallisation of SiC from the amorphous phase.

Table 2
Radii of diffraction rings R and corresponding distances of atomic planes, d, and respective (hkl)-planes of β-SiC nucleated in poly(hydridomethyl)silazane-derived silicon carbonitride annealed at 1450°C for 50 h in nitrogen

Number of diffraction rings	Radius R (mm)	d (Å)	(hkl)
1	8.4 ± 0.3	2.58 ± 0.09	(111)
2	13.7 ± 0.3	1.57 ± 0.04	(220)
3	16.0 ± 0.4	1.35 ± 0.04	(311)

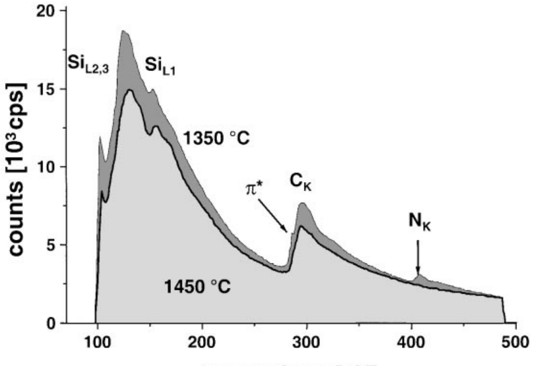


Fig. 9. Electron energy-loss (EELS) spectra of Si–C–N ceramics in dependence of the annealing temperature T_a (holding time 50 h in 0.1 MPa N_2).

Table 3
Phase composition of poly(hydridomethyl)silazane-derived Si–C–N ceramics subsequently annealed at the given temperature in N_2 ($t_a = 50$ h)

	Phase	Fraction (vol%)	Description
As-Synthesised at 1000°C:	pores	16	
	a-SiCN	84	$Si_{1.7}C_{1.0}N_{1.5}$ (amorphous)
After Annealing at 1450°C :	pores	12	
	β-SiC	ca. 16	Nano-crystalline
	α-Si_3N_4	≈10–20	Micro-crystalline
	a-SiC(N)	≈55–65	Amorphous

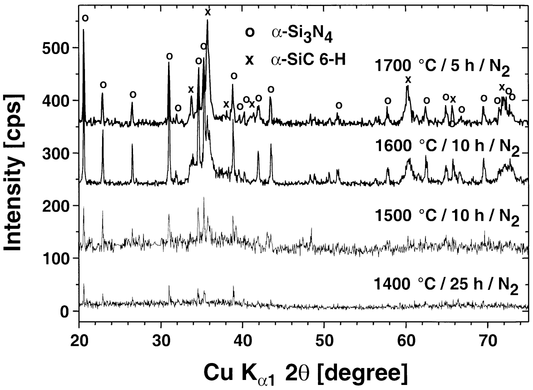


Fig. 10. X-ray diffraction pattern of Si–C–N ceramics in dependence of the annealing temperature T_a in 0.1 MPa N_2.

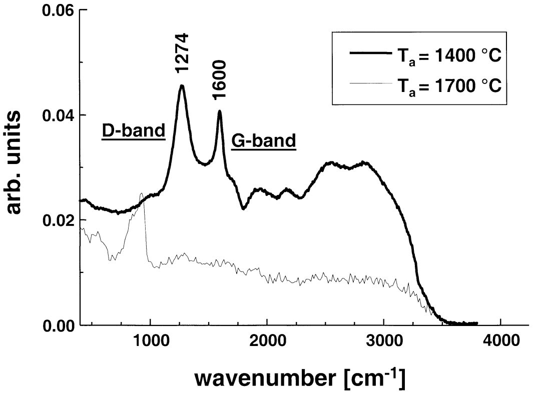
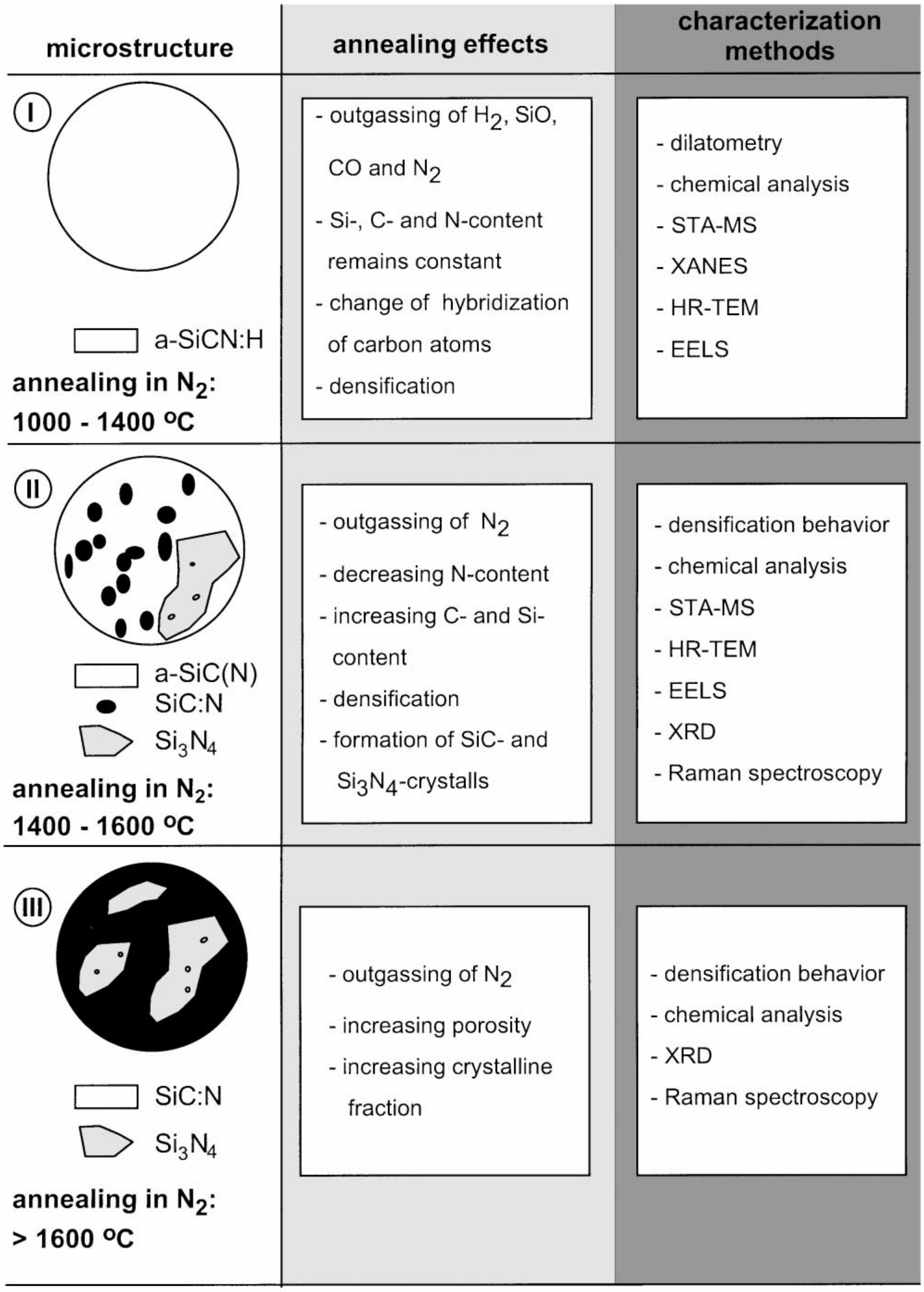


Fig. 11. Raman spectra of Si–C–N ceramics in dependence of the annealing temperature T_a in 0.1 MPa N_2.

Finally, the total fraction of crystalline phases increases at $T > 1450°C$ due to the decomposition of the amorphous Si–C–N–phase. At 1700°C the ceramic is completely crystallised and contains no amorphous phases as discussed in the next section.

3.7. Raman spectroscopy

Raman spectroscopy was used to detect sp^2-hybridised carbon. Characteristic peaks in the Raman spectrum can be observed at wave numbers of 1600 and 1280 cm^{-1}, which are described as graphite band (*G*) and defect band (*D*), respectively.[22] Fig. 11 depicts the Raman spectra of Si-C-N ceramics heat treated at different temperatures. It is evident that the *G*- and *D*-bands are found up to 1600°C annealing temperature. However, after annealing at 1700°C the characteristic graphite peaks have disappeared indicating that silicon carbonitride contains no sp^2-hybridised carbon atoms neither in form of a remaining amorphous phase nor in crystalline form.



microstructure	annealing effects	characterization methods
Ⓘ ▭ a-SiCN:H **annealing in N_2: 1000 - 1400 °C**	- outgassing of H_2, SiO, CO and N_2 - Si-, C- and N-content remains constant - change of hybridization of carbon atoms - densification	- dilatometry - chemical analysis - STA-MS - XANES - HR-TEM - EELS
Ⓘⓘ ▭ a-SiC(N) ● SiC:N ▱ Si_3N_4 **annealing in N_2: 1400 - 1600 °C**	- outgassing of N_2 - decreasing N-content - increasing C- and Si-content - densification - formation of SiC- and Si_3N_4-crystalls	- densification behavior - chemical analysis - STA-MS - HR-TEM - EELS - XRD - Raman spectroscopy
Ⓘⓘⓘ ▭ SiC:N ▱ Si_3N_4 **annealing in N_2: > 1600 °C**	- outgassing of N_2 - increasing porosity - increasing crystalline fraction	- densification behavior - chemical analysis - XRD - Raman spectroscopy

Fig. 12. Schematic illustration of the microstructural development of poly(hydridomethyl)silazane-derived silicon carbonitride ceramic in the temperature range between 1000 and 1700°C.

4. Conclusion

The investigations reported here reveal that the microstructure and composition of poly(hydridomethyl)silazane-derived Si–C–N-ceramics strongly depend on the annealing conditions. The microstructural development is schematically depicted in Fig. 12 and can be summarised as follows:

1. Apart from few isolated Si_3N_4-grains formed at 1350°C, amorphous silicon carbonitride is found in the temperature range between 1000 and 1400°C, exclusively (microstructure I). The amorphous ceramic contains residual hydrogen and is, therefore, denoted as a-SiCN:H. Although gaseous species like H_2, SiO, CO and N_2 are evolved during annealing of the ceramic material between 1000 and 1400°C, the overall composition remains unchanged. However, the hydrogen content decreases from 5 at% at 1000°C down to 1 at% at 1300°C. The loss of hydrogen leads to the formation of sp^2- rather than sp^3-hybridised carbon atoms. These rearrangements together with the decreasing porosity are responsible for the densification of the material in this temperature range. Hence, the Si–C–N bulk density increases with increasing annealing temperature while the solid state density of about 2.3 g/cm^3 remains constant.
2. In the temperature range between 1400 and 1600°C (microstructure II in Fig.12) the main outgassing species is N_2. Therefore, the N-content decreases, and the C- and Si-content increase. Again, the solid phase density is enhanced due to a pronounced mass loss and beginning crystallisation of the Si–C–N-ceramic. Besides Si_3N_4 nano-crystalline SiC is found. Moreover, the nano-sized SiC grains form percolation paths throughout the ceramic matrix. The crystalline phases are identified as α-Si_3N_4, and β-SiC at 1450°C and as α-Si_3N_4 and α-SiC (6H) at $T > 1500$°C. The overall crystalline fraction increases with growing temperature and gives higher solid state densities. The molar ratio of Si_3N_4 to SiC decreases at higher temperatures which is caused by the reaction of Si_3N_4 and "free" carbon partitioned from the amorphous matrix forming SiC and N_2. The residual amorphous SiC(N)-phase contains reduced nitrogen contents and a reduced fraction of sp^2-hybridised carbon. Consequently, the composition and structure changes from an amorphous SiCN matrix towards that of polycrystalline SiC and Si_3N_4 after completed crystallisation.
3. Above 1600°C (microstructure III in Fig. 12), no sp^2-carbon containing phases were detected in the ceramic by Raman spectroscopy supporting that the amorphous phase has completely transformed to a polycrystalline composition. The resulting material is comprised of SiC and Si_3N_4, exclusively. Due to the loss of N_2 during the high temperature annealing the open porosity is significantly increased compared to that of microstructure II in Fig. 12 leading to a lower bulk density.

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