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# Structure Analysis and Properties of Si-C-N Ceramics Derived from Polysilazanes

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Dedicated to Professor Dr. MANFRED RÜHLE on the occasion of his 60th birthday

Pyrolysis of different polysilazanes has been used to prepare novel covalent amorphous ceramics composed of silicon, carbon, and nitrogen. The formation and structure of the as-pyrolyzed amorphous state and its devitrification into stable crystalline phases have been investigated by means of nuclear magnetic resonance spectroscopy, infrared spectroscopy, thermogravimetry, mass spectroscopy, X-ray and neutron diffraction, and by transmission electron microscopy. Additionally, the electrical conductivity and the compression creep behaviour of the as-received materials have been analyzed.

## 1. Introduction

Silicon nitride, silicon carbide and silicon nitride/carbide-based composites are suitable candidates for high temperature applications because of their high thermal, chemical and mechanical stability. One possibility for the preparation of such ceramics is liquid phase sintering of silicon nitride and/or carbide powders in the presence of oxidic additives, like  $Al_2O_3$  and  $Y_2O_3$  [1 to 3]. Since during the densification process these sintering aids vitrify and segregate at the grain boundaries they can lead to a deterioration of the mechanical and chemical stability of sintered materials at elevated temperatures due to softening and enhanced oxygen diffusion, respectively, provided by their glassy nature. Therefore, current research activities with respect to high temperature applications of such materials focus on the development of powder technology routes which allow the reduction or even the elimination of the fraction of additives.

A proper route of a sinter aid-free preparation of carbide/nitride ceramics is the pyrolysis of preceramic polymers [4 to 8]. The main aim of this processing route is the architectural design of ceramics on the basis of molecular units in order to control the structure and the properties of such materials on an atomic scale. According to this route the preceramic polymers are at first transformed into amorphous ceramics by pyrolysis at temperatures dependent on their chemical composition and molecular structure. With a subsequent heat treatment at higher temperatures such amorphous solids can be crystallized into thermodynamically stable phases. Synthesis and thermal treatment of the precursor polymers allow the control of their physical and chemical properties providing processing opportunities for the preparation of ceramic fibers, films or monoliths without using sintering aids.

This paper describes the synthesis of silicon nitride/carbide-based ceramics by pyrolysis of polyhydridomethylsilazane (PHMS) and polyvinylsilazane (PVS). It is the aim of this paper to combine experimental results of different previous studies [9 to 15] and recent unpublished data in order to present a comprehensive description of the structure formation during ceramization and crystallization of these two commercially available polysilazanes. Additionally, recent results on electrical conductivity measurements [16] and on compression creep tests [17, 30] of ceramics derived from these precursors are reported.

#### 2. Experimental

The structure units of both polymers used for the preparation of Si-C-N ceramics are shown in Figs. 1 and 2. PHMS (NCP 200, Nichimen Corp., Japan) is a copolymer of methyl- and dimethylsilazane units in the ratio 2:1 (calculated from the corresponding peak areas in the <sup>29</sup>Si NMR spectrum). PVS (VT 50, Hoechst AG, Germany) consists of vinylsilazane units and about 10%-N(CH<sub>3</sub>)<sub>2</sub> end group units [18].

In order to form preceramic networks which do not melt during pyrolysis the as-received polymers were crosslinked at 400 °C for 4.5 h (PHMS) or at 240 °C for 2 h (PVS) and subsequently milled and sieved (28  $\mu$ m screen). The resulting powders subsequently were compacted either by cold-isostatic pressing at 635 MPa or by pressing at elevated temperature (plastic forming) [9] using a maximum pressure of 47.75 MPa and temperatures of 275 °C (PHMS) or 250 °C (PVS). For pyrolysis the cold or warm compacted samples were placed in quartz tubes in a slight argon flow and heated with a heating rate of 25 K/h up to different temperatures (350, 550, 625, 700 or 1050 °C) which were held for 4 h.

By cold-isostatic pressing and subsequent pyrolysis amorphous ceramics with a porosity of 10 to 15% (determined by mercury porosimetry) were obtained. If plastic forming was applied the green density could be increased and the porosity of the as-pyrolyzed material thereby reduced to 3%.

For crystallization studies the as-pyrolyzed materials were heat treated in  $N_2$  atmosphere for 5 to 50 h at different temperatures in the range of 1200 to 1450 °C (heating rate: 120 K/h).

The Nuclear Magnetic Resonance Spectroscopy (NMR) experiments were performed on a Bruker 300 MSL spectrometer [11]. The resonance frequency for <sup>1</sup>H was 300.13 MHz, for <sup>13</sup>C 75.47 MHz and for <sup>29</sup>Si 59.60 MHz. All spectra were acquired using



Fig. 1. Structure units of the PHMS polymer



Fig. 2. Structure units of the PVS polymer

magic angle spinning (MAS) with a rotation frequency of 4.5 kHz. The excitation of the observed nucleus was 3  $\mu$ s for <sup>1</sup>H, 4  $\mu$ s for <sup>13</sup>C and 5  $\mu$ s for <sup>29</sup>Si. All spectra were <sup>1</sup>H-decoupled during the data acquisition. The samples were also measured with a crosspolarization sequence (CP). The contact time for <sup>13</sup>C and <sup>29</sup>Si was 1 and 5 ms, respectively. The repetition time was 10 s.

The Infrared Spectroscopy (IR) investigations were performed on a Bruker FT-IR IFS 66 using diffuse reflexion technique (powder samples).

The Thermogravimetry and Mass Spectrometry (TG/MS) investigations were performed on a Netzsch 409/429-403 machine in vacuum. The heating rate was 5 K/min up to 1200 °C.

The X-ray wide angle scattering was done in transmission mode using  $AgK_{\alpha}$  radiation [12].

The neutron wide angle scattering experiments were performed at the ISIS facility of the Rutherford Appleton Laboratory, UK, using the SANDALS instrument [12]. There, a range of wave vector transfer up to 25 Å<sup>-1</sup> could be measured. This is essential for the resolution of the radial distribution function in real space. Neutron small angle scattering was performed at the BENSC facility of the HMI, Berlin, using the V4 instrument. The neutron wavelength was 8 Å [12].

For the *Transmission Electron Microscopy (TEM)* investigations were performed with specimens fabricated by standard preparation techniques (mechanically sectioning the materials, polishing and dimpling the 3 mm discs, which was followed by a final Ar ion beam thinning). The specimen were characterized by conventional (CTEM), energy filtering (EFTEM) and high resolution TEM (HRTEM). For the studies a Zeiss EM 912 Omega and a JEOL 4000EX were used [10].

Besides various conventional TEM methods two dimensional elemental distribution images in the electron spectroscopic imaging (ESI) technique have been proven to be an important tool for the characterization of the chemical microstructure in large specimen areas (several  $\mu m^2$ ) at high resolution (2 to 3 nm) within short times [19 to 22].

*Electrical conductivity* measurements were done with cold compacted and pyrolyzed samples by means of two point measurements in a temperature range from room temperature up to 500  $^{\circ}$ C [16]. The device used consists of a high temperature furnace (GERO), a measuring cell unit (made of quartz glass), a measuring device for voltage and current (Keithley 236), a temperature measuring device (THERM 2281-8), and a computer.

For the measurements the as-pyrolyzed samples were cut and ground into rectangular shaped bars. In order to ensure the electrical contact between the material and the platinum electrodes a 3000 Å thick platinum film was deposited onto the two surfaces per-

pendicular to the longitudinal axis of the samples by sputtering. Subsequently, the samples were placed into evacuated quartz glass cells. The temperature and its gradient along the longitudinal axis of the sample were measured by two thermocouples placed at both ends of the sample. The thermoelectric voltage applied to the sample is read into the computer through an analog-digital converter.

For the determination of the sample conductivity, a voltage is applied to the sample and the resulting current read into the computer through the serial IO port. A control program is used to determine the electrical resistance of the sample and to plot the electrical conductivity against the sample temperature.

Compression creep studies [17, 30] have been done with material densified by plastic forming and subsequent pyrolysis. The test specimen were cut and ground into rectangular bars with a height of 7.5 mm and with a cross sectional area of  $1.5 \times 1.5$  mm<sup>2</sup>. The small cross sectional area was chosen because stresses up to 250 MPa were applied and the maximum load of the creep apparatus was limited to 1000 N at high temperatures. The height of the specimen was also limited to avoid buckling of the specimen. A square cross sectional area was chosen to facilitate the preparation of the specimen.

A spring loaded creep apparatus (Amsler DSM 6101) with a 1600 °C furnace (Maytec Achtkantofen) was used for the testing. Inside the furnace alumina push rods and silicon carbide load pads were used to apply the testing force. A spiral spring was used for the loading. The strain of spring was measured by a linear potentiometer and the testing force was calculated from the strain of the spring. An accuracy of  $\pm 1$  N was achieved for the force measurements. Two SiC scanning pins placed at the upper load pad and another scanning pin at the lower load pad were used to measure the length change of the specimen. The scanning pins were connected to an inductive strain gage with a resolution of 0.1 µm in the cold part of the testing machine.

Testing was done in air at temperatures of 1450, 1500 or 1550 °C. The temperature was measured with PtRh(10)/Pt thermocouple which was placed at a distance of about 2 mm from the specimen. The specimens were heated up to the testing temperature as fast as possible using the maximum power of the furnace to avoid oxidation at intermediate temperatures. The heating ramp for tests at 1550 °C is shown in Fig. 3.



Fig. 3. Heating ramp used for creep tests at 1550 °C

During the heating a clamping force of about 2 N was applied to the specimen. To get the displacement measuring system into thermal balance after test temperature was reached, the creep stress was not applied until 30 min. The loading of the specimen took 30 s. The strain measurement was started after reaching the creep stress.

## 3. Structure Formation

The structure and phase formation during ceramization and crystallization of preceramic compounds is very much dependent on the composition and molecular structure of the precursor. Fig. 4 shows the composition of the ceramics obtained by pyrolysis of PHMS and PVS at 1050 °C within isothermal sections of the Si–C–N phase diagram valid up to a) 1438 °C and b) between 1438 and 1876 °C.

As can be seen from this figure (crystalline)  $Si_3N_4$ , SiC and C form a three-phase equilibrium which is stable up to 1438 °C. Above this temperature  $Si_3N_4$  is unstable next to C, thus decomposition occurs by loss of nitrogen according to the equation

$$\mathrm{Si}_{3}\mathrm{N}_{4} + 3 \mathrm{C} \to 3 \mathrm{Si}\mathrm{C} + 2 \mathrm{N}_{2} . \tag{1}$$

I.e., at temperatures above 1438 °C the ceramics decompose into SiC and C or SiC and  $Si_3N_4$  depending on their composition.

According to these phase equilibria the pyrolysis of PVS should result in the formation of a two-phase material consisting of  $Si_3N_4$  and C whereas the ceramization of PHMS should lead to a material composed of  $Si_3N_4$ , SiC and C. At 1438 °C both materials should transform into SiC/C and  $Si_3N_4$ /SiC composites, respectively combined with a loss of nitrogen. At 1876 °C and ambient pressure  $Si_3N_4$  dissociates into nitrogen and liquid Si.



Fig. 4. Isothermal section of the ternary system Si–C–N. a) below 1438 °C and b) in the temperature range between 1438 and 1876 °C [23]. The compositions of the ceramics obtained by pyrolysis of the polysilazanes PHMS ( $\blacksquare$ ) and PVS ( $\bigcirc$ ) at 1050 °C are inserted



Fig. 5.  $^{13}\mathrm{C}\text{-NMR}$  spectra of PHMS at different annealing temperatures up to 1050  $^{\circ}\mathrm{C}$  [11]

#### 3.1 Ceramization

The ceramization of the crosslinked PHMS and PVS, i.e. the structure formation during their pyrolysis has been studied by NMR, IR, TG/MS, X-ray and neutron diffraction.

# 3.1.1 Polysilazane PHMS

The results of the NMR investigations [11] are summarized in Figs. 5 and 6, those of the IR investigations in Fig. 7, and those of the X-ray and neutron diffraction studies [12] in Figs. 8 and Fig. 9.

The results of these investigations reveal the reaction process of ceramization as shown in Fig. 10.

In detail the results can be explained as follows: The NMR <sup>13</sup>C spectrum of the polymer (Fig. 5) shows a peak at 5 ppm which is assigned to the  $Si-\underline{CH}_3$ group. The <sup>29</sup>Si spectrum of the polymer (Fig. 6) shows three signals. The peaks at -22 ppm and -5 ppm are caused by <u>SiN<sub>2</sub>CH and SiN<sub>2</sub>C<sub>2</sub> environments</u>, respectively, within a six-membered cyclosilazane ring. The peak at -14 ppm is assigned to the bridging <u>SiN<sub>3</sub>H</u> sites in the six-membered ring.

The IR spectroscopy of the polymer (Fig. 7) shows signals which are assigned to N-H  $(3405 \text{ cm}^{-1})$ , C-H

(2960 to 2910 cm<sup>-1</sup>) and Si-H (2130 cm<sup>-1</sup>) [24] and signals of SiC-H (1265 and 1405 cm<sup>-1</sup>), Si<sub>2</sub>N-H (1180 cm<sup>-1</sup>) and Si-CH<sub>2</sub>-Si (1035 cm<sup>-1</sup>) (caused by a small amount of CH<sub>2</sub> bridges obtained by crosslinking reactions described below).

The structure of the polymer based on both the NMR and IR results is shown in Fig. 11. The structure consists of crosslinked six-membered rings as proven by the results of the <sup>29</sup>Si NMR spectrum of the polymer (see above).

The NMR as well as the IR spectra of the product heated up to 350 °C mainly remained unchanged as compared to those of the as-received polymer.



Fig. 6.  $^{29}$ Si–NMR spectra of PHMS at different annealing temperatures up to 1050 °C [11]

At 550 °C in the NMR <sup>13</sup>C spectrum (Fig. 5) an additional peak at 12 ppm is found as a shoulder. This is attributed to  $\underline{CH}_2$  bridges which were formed by a crosslinking reaction of the methyl groups with the hydrogen of Si-H (2) or C-H (3) groups:

$$-CH_3 + H - Si \equiv \rightarrow -CH_2 - Si \equiv + H_2 , \qquad (2)$$

$$-CH_3 + CH_3 - Si \equiv \rightarrow -CH_2 - Si \equiv + CH_4.$$
(3)



Fig. 7. IR spectra of PHMS at different annealing temperatures up to 1050 °C

The occurrence of these reactions is supported by means of TG/MS investigations which show an evaporation of methane in the temperature range between 400 and 800 °C and of hydrogen between 350 and 1050 °C, respectively. The same is true for the IR investigations which show with increasing temperature decreasing signals assigned to N–H, C–H, Si–H, SiC–H, Si<sub>2</sub>N–H, and Si–CH<sub>2</sub>–Si (Fig. 7).

The <sup>29</sup>Si spectrum at 550 °C (Fig. 6) shows also a broadening of the lines. This broadening is due to a modification of the environment of the Si atoms caused by the crosslinking reaction (see Fig. 10). The signals of the <u>Si</u>N<sub>2</sub>CH and the <u>Si</u>N<sub>3</sub>H sites combine. The number of <u>Si</u>N<sub>2</sub>C<sub>2</sub> sites were increased at the expense of the <u>Si</u>N<sub>2</sub>CH sites which can be detected by calculating of the appropriate peak areas (the signal was fitted with three peaks to estimate the several components). The ratio of <u>Si</u>N<sub>2</sub>C<sub>2</sub> and <u>Si</u>N<sub>2</sub>CH has changed from 1:2 (polymer) to 1:1 (550 °C product) indicating that the crosslinking reactions mentioned above ((2) and (3)) occur preferably via the reaction of Si–H groups with methyl groups which leads to the formation of H<sub>2</sub>. This is in accordance with the MS investigations which reveal that the evaporation of H<sub>2</sub> starts at lower temperatures compared to the formation of methane caused by the reaction of Si–C groups with methyl groups.



Fig. 8. Total pair correlation functions, a) from X-ray diffraction, b) from neutron diffraction [12]

During heating up to 625 °C the successive increase of the chemical shift in the <sup>13</sup>C spectrum (Fig. 5) continued, caused by the increased coordination of the C atoms with Si atoms (Si-<u>C</u>H<sub>3</sub>: 5 ppm; Si-<u>C</u>H<sub>2</sub>-Si: 12 ppm; Si<sub>2</sub>-<u>C</u>H-Si: 18 ppm; Si<sub>4</sub>C: 24 ppm). In



the <sup>29</sup>Si spectrum (Fig. 6) a signal at -43 ppm is detected which is assigned to SiN<sub>4</sub> sites. These sites were formed by crosslinking reactions of the NH groups with Si–H and Si–CH<sub>3</sub> groups, respectively (see Fig. 10). Moreover, TG/MS investigations showed an evaporation of a small amount of ammonia between 500 and 650 °C. This is caused by the transamination reaction

$$3 \text{ H-NSi}_2 \rightarrow 2 \text{ NSi}_3 + \text{NH}_3$$
. (4)

Fig. 9. Gaussian fitting to the peak at 1.74 Å of the RDF(r)-function corresponding to  $G_n(r)$  from Fig. 8 [12]



Thus, the coordination of the Si atoms with N atoms and vice versa increases successively.

At 1050 °C, i.e. after complete ceramization, the <sup>13</sup>C spectrum (Fig. 5) shows a broad signal with a maximum located at 24 ppm which is assigned to  $\text{Si}_4\underline{\text{C}}$  sites that can be considered as structural units of silicon carbide. The <sup>29</sup>Si spectrum (Fig. 6) remains in general unchanged compared to the 625 °C product. The crosslinking reactions continued and additional SiN<sub>4</sub> units were formed which are the basic structure units of Si<sub>3</sub>N<sub>4</sub>. Broad signals centered at -25 and -15 ppm as a shoulder are still found in the 1050 °C products which confirm the existence of Si units containing Si-C bonds.

The short-range ordering and structural units which build up the amorphous as-pyrolyzed ceramic network as have been revealed from NMR studies have been confirmed by X-ray and neutron scattering [12]. Wide angle scattering did not indicate any traces of crystalline peaks but distinct information on short-range ordering. Fig. 8 shows the pair correlation functions G(r) deduced by Fourier transformation from the measured total X-ray and neutron structure factor of the as-pyrolyzed material.



With X-rays in the pair correlation function  $(G_x(r))$  two distinct peaks at 1.73 and 2.98 Å are observed (Fig. 8a), whereas in the neutron pair correlation function  $G_n(r)$  four peaks at 1.37, 1.74, 2.46 and 2.85 Å are displayed (Fig. 8b).

Fig. 11. Structure of the PHMS polymer

The peaks at 1.37 and 2.46 Å in  $G_n(r)$  belong to C–C and C–(C)–C correlations, respectively. With X-rays these peaks are not observed due to the much smaller weighting factor. Note that the peak positions are in good agreement with the distances in graphite at 1.42 and 2.46 Å. Thus, it can be concluded that the investigated ceramics include amorphous graphite-like carbon.

The peak at 1.74 Å reflects the Si–N bonds. It appears with about the same height in  $G_{\rm x}(r)$  and  $G_{\rm n}(r)$ . The peak at 2.85 Å in  $G_{\rm n}(r)$  is attributed to a N–(Si)–N correlation, and the one at 2.98 Å in  $G_{\rm x}(r)$  to a Si–(N)–Si correlation. All three peaks are in good agreement with those of the corresponding distances of crystalline Si<sub>3</sub>N<sub>4</sub>.

Nevertheless, the positions of the peaks at 1.74 and 2.85 Å are shifted slightly to larger values of r and they are broadened at the right hand side compared to pure  $Si_3N_4$ . Considering that in crystalline SiC a direct Si–C distance appears at 1.89 Å and an indirect C–(Si)–C distance at 3.06 Å this suggests that in the investigated ceramics there is also a considerable number of Si–C bonds.

Fig. 9 shows the peak at 1.74 Å in the total radial distribution function  $\text{RDF}(r) = 4\pi r^2 \rho_0 + rG_n(r)$  ( $\rho_0$  is the atomic density) fitted by the sum of two Gaussian curves at 1.74 and 1.83 Å. Note, that the position of the peak in this plot is shifted to 1.76 Å caused by the calculation of the RDF.



Fig. 12. TEM bright field image (left part) and diffraction pattern (right part) of siliconcarbonitride obtained from a PHMS precursor after pyrolysis at 1050  $^{\circ}\mathrm{C}$ 

From the areas of the Gaussian curves the average coordination numbers  $Z_{\text{Si-N}} = 3.0$ and  $Z_{\text{Si-C}} = 1.0$  were obtained. The sum  $Z_{\text{Si}} = Z_{\text{Si-N}} + Z_{\text{Si-C}} = 4.0$  proves that in the amorphous ceramics the Si atoms are tetrahedrally coordinated which is in good agreement with the NMR results. It should be noted however that on the basis of the average values of Z it cannot be distinguished between the existence of SiN<sub>4</sub> and SiC<sub>4</sub> tetrahedra only and the additional existence of tetrahedra mixed in C and N (Si(C, N)<sub>4</sub>).

Despite this extended ordering the as-pyrolyzed material is fully amorphous. This is in accordance not only with wide angle X-ray and neutron diffraction studies but also with structural and analytical transmission electron microscopy investigations which did not show any crystalline precipitates. This is shown by bright field images (Fig. 12), selected area diffraction, and electron spectroscopic imaging (Fig. 13).

Elemental distribution images of the elements Si, C and N did not show any indication of the occurrence of segregation on a scale above the resolution limit of about 2 nm



Fig. 13. Elemental distribution images for carbon (above, left), nitrogen (above, right) and silicon (below, left) obtained with the electron spectroscopic imaging (ESI) technique of a PHMS-derived ceramic prepared at 1050  $^{\circ}$ C



Fig. 14. High resolution micrograph of the amorphous PHMS-derived Si–C–N ceramic obtained at 1050  $^{\circ}$ C. The contrast of the high resolution micrograph shows the typical appearance known from perfectly amorphous materials

(Fig. 13). However, the formation of small clusters or crystallites with composition close to the average composition of the material could not be excluded from these studies. Therefore, high resolution microscopy was employed which would reveal structural inhomogeneities on a subnanometer scale. Fig. 14 shows the high resolution micrograph of a 1050 °C sample with contrast variations typical for an amorphous material and with no indication of the formation of crystallites or crystalline precipitates.



Fig. 15. Amorphous PHMS-derived Si–C–N ceramic; formation of amorphous Si<sub>3</sub>N<sub>4</sub> regions during annealing. a) volume fraction, b) radius.  $\Box$  1050,  $\odot$  1200,  $\triangle$  1300,  $\nabla$  1400, +1450 °C. The origin of the time scale refers to the point in the heating curve where the indicated temperature was reached, i.e. it involves the heating ramp [12]

In order to gain more insight into the medium range order of the amorphous materials, small angle scattering has been applied to study fluctuations of the composition and density which exhibit a size below the scale of the detection limit of the ESI technique. In this connection small angle neutron scattering (SANS) cross sections show, that the material contains inhomogeneities which give rise to an observed SANS signal [12]. The measured SANS effect has to be attributed to an amorphous silicon nitride phase, segregated into a Si–C–N matrix due to the values determined for the difference of the scattering length densities of the segregations and the matrix. Fig. 15 indicates that the



material contains already in the aspyrolyzed stage, i.e. after heat treatment at 1050 °C inhomogeneities in the size range of 1.2 to 1.4 nm.

Keeping in mind the wide angle scattering results these inhomogeneities were suggested to consist of amorphous Si<sub>3</sub>N<sub>4</sub>, SiC and C phases.

#### 3.1.2 Polysilazane PVS

The results of NMR investigations [13] are summarized in Figs. 16 and 17 and those of the IR investigations in Fig. 18. From these results the ceramization process as shown in Fig. 19 has been deduced.

The results are in detail as follows: In the <sup>13</sup>C spectrum of the polymer (Fig. 16) beside two spinning side bands at around 200 and 75 ppm three peaks are detected. The two major peaks at 142 and 132 ppm are caused by the C=C bonding (sp<sup>2</sup>-hybridized carbon). The signal between 20 and 40 ppm is assigned to a small amount of sp<sup>3</sup>hybridized carbon. It is caused by the -N(<u>C</u>H<sub>3</sub>)<sub>2</sub> end groups.

The <sup>29</sup>Si spectrum of the polymer (Fig. 17) shows two peaks: the sig-

Fig. 16.  $^{13}\mathrm{C}\text{-NMR}$  spectra of PVS at different annealing temperatures up to 1050  $^{\circ}\mathrm{C}$ 



nal at -20 ppm is caused by a  $\underline{Si}N_3C(sp^3)$  environment (polymerized vinyl groups) and the peak at -35 ppm is assigned to a  $\underline{Si}N_3C(sp^2)$  environment.

For the product heated up to 250 °C the NMR spectra mainly remained unchanged. After heating up to 350 °C the <sup>13</sup>C spectrum (Fig. 16) shows only a small amount of C=C groups, i.e. sp<sup>2</sup> carbon and a strongly increased number of sp<sup>3</sup> carbon. With increased temperature more and more vinyl groups are polymerized and form CH<sub>2</sub> bridges (sp<sup>3</sup>) (see Fig. 19). Thus,



Fig. 18. IR spectra of the ceramization of PVS at different annealing temperatures up to 1050 °C

the peak at 25 ppm resulting from the  $\underline{CH}_2C_2$  groups [25] combines with the signal of the  $-N(\underline{CH}_3)_2$  end groups. An additional signal at 5 ppm is found as a shoulder which is due to the  $\underline{CH}C_2Si$  groups [25]. This is confirmed by the corresponding <sup>29</sup>Si spectrum (Fig. 17) which shows an increased signal of  $\underline{Si}N_3C(sp^3)$  and a decreased peak of  $\underline{Si}N_3C(sp^2)$ .

Compared to the 350 °C product the <sup>13</sup>C spectrum of the 550 °C product (Fig. 16) exhibits an increased signal of sp<sup>2</sup> carbon and a decreased signal of sp<sup>3</sup> carbon. Moreover, this transformation of the carbon atoms is accompanied by the evaporation of H<sub>2</sub>, which begins at 350 °C and can be still detected at 550 °C by MS. Thus, these results indicate that hydrogen is removed from the hydrocarbon chains leaving behind sp<sup>2</sup> (graphite-like) carbon (see Fig. 19). Simultaneously, the sp<sup>3</sup> carbon signal is split into two peaks centered at 5 and 25 ppm, respectively. They are due to the two different kinds of sp<sup>3</sup> carbon mentioned above: with and without Si–C bonds, respectively. If the temperature was raised further to 625 °C these signals completely disappear due to a strong decrease of the number of Si–C bonds and of the sp<sup>3</sup> carbon content. These results are in accordance with the MS investigations and the <sup>29</sup>Si spectra of the 550 and 625 °C products. Owing to the <sup>29</sup>Si spectra the signal attributed to <u>SiN<sub>3</sub>C(sp<sup>3</sup>) sites decreases</u>. Moreover, an increasing content of <u>SiN<sub>4</sub> sites (-42 ppm) can be detected</u>. These results indicate a transformation of



Fig. 19. Mechanisms suggested for the ceramization of the polysilazane PVS

 $\underline{SiN_3C(sp^3)}$  into  $\underline{SiN_4}$  sites connected with a separation of carbon and Si/N-containing units. Additionally, the MS studies reveal the evaporation of methane in the temperature range between 400 °C and 600 °C which leads to a further decrease of the sp<sup>3</sup> carbon content and can be attributed to the removal of the N(CH<sub>3</sub>)<sub>2</sub> end groups.

If the temperature was raised up to  $1050 \,^{\circ}$ C the <sup>13</sup>C spectrum (Fig. 16) shows only the signal of sp<sup>2</sup> carbon. The peak in the <sup>29</sup>Si spectrum (Fig. 17) centered at -40 ppm is assigned to a <u>SiN<sub>4</sub></u> environment [13]. Furthermore, the evaporation of a small amount of ammonia between 700 and 800 °C can be detected by MS and can be assigned to the transamination reaction mentioned above (4) yielding NSi<sub>3</sub> units.

The IR investigations (Fig. 18) confirm the NMR results. With increasing temperature the signals assigned to N–H (3375 cm<sup>-1</sup>), to C–H (methyl group: 3045 to 2900 cm<sup>-1</sup>, vinyl group: 1915, 1405 and 1010 cm<sup>-1</sup>) and to C=C (1595 cm<sup>-1</sup>) [24] decrease. The Si–N signal is found at 980 cm<sup>-1</sup>. The SiC–H signal (1225 cm<sup>-1</sup>) decreases during ceramization. Moreover, at temperatures above 350 °C the signal of Si–H (2150 cm<sup>-1</sup>) is

detected. As a consequence dehydrogenation between Si–H and N–H groups can occur leading to an increased coordination of Si with N atoms which is in accordance with the above-mentioned NMR results as well as with MS studies that show the evaporation of hydrogen between 350 and 1050  $^{\circ}$ C.

The ceramization process can be summarized as follows (Fig. 19): The first step is the polymerization of vinyl groups resulting in the formation of carbon chains (sp<sup>3</sup> hybridized carbon). In the temperature range between 550 and 625 °C the Si–C bonds disappear and Si–N bonds are formed. As Fig. 19 shows there are two possible ways for these reactions: a) splitting of carbon chains leaving behind Si–H bonds which can react with NH groups resulting in the formation of Si–N bonds and evaporation of H<sub>2</sub> and b) direct reaction of the Si–C bonds with NH groups. Reaction a) is confirmed by the IR spectra which show the presence of Si–H bonds at temperatures above 350 °C.

#### 3.2 Crystallization

#### 3.2.1 PHMS-derived material

During annealing above the pyrolysis temperature the amorphous stage of the as-pyrolyzed material is fully maintained. Elemental distribution images still show a completely



Fig. 20. Bright field image of the PHMS-derived Si–C–N ceramic after heat treatment at 1350 °C. First crystalline segregations  $(Si_3N_4)$  can be detected in the still amorphous Si–C–N matrix

homogeneous distribution of the elements. However, according to small angle neutron scattering results, there occurs both an increase of the volume fraction and a coarsening of the segregations observed in the amorphous as-pyrolyzed stage during annealing at this temperature and with further temperature increase up to  $1400 \,^{\circ}\text{C}$  (Fig. 15). The dashed lines were fitted using a Gibbs-Evetts-Leake type of annealing function [26]. In the temperature range around 1200 to  $1300 \,^{\circ}\text{C}$  the increase in volume of the segregation is faster than at temperatures as high as  $1400 \,^{\circ}\text{C}$ . It is to note that at this temperature the state of equilibrium is not attained within the time interval of 15 h.

The temperature-time dependence of the radius R of the scattering regions in Fig. 15b shows an increase from 1.2 nm in the as-pyrolyzed ceramic up to about 2.5 nm after a 15 h anneal at 1400 °C.

At 1450 °C a decrease of the volume fraction v of the segregated Si<sub>3</sub>N<sub>4</sub> phase can be detected [14]. It is to note that the decrease of v at 1450 °C in Fig. 15a is not associated





Fig. 21. Elemental distribution images of the material obtained from PHMS after crystallization at 1500  $^{\circ}\mathrm{C}$ 

with a decrease of R. This behaviour is explained by the facts that on the one hand the decomposition affects first the smaller Si<sub>3</sub>N<sub>4</sub> regions, whereas on the other hand the size R, as established from small angle scattering, generally is associated mainly with the larger regions.

The reduction of the volume fraction of  $Si_3N_4$  at 1450 °C corresponds completely with the phase equilibria shown in Fig. 4, since for temperatures above 1438 °C the  $Si_3N_4$ content of the PHMS-derived ceramic is reduced according to (1).

In transmission electron microscopy studies at annealing temperatures of  $1350 \,^{\circ}\text{C}$  first isolated areas containing crystalline  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> grains and free carbon were detected (Fig. 20).

An increase in length or temperature of the heat treatment increases the amount of crystallinity.

Annealing of the material at 1500 °C yields a completely crystalline material consisting of  $Si_3N_4$  and SiC. The microstructure of which is characterized by nanocrystalline SiC grains embedded in a microcrystalline matrix of  $Si_3N_4$  (Fig. 21).



Fig. 22. Amorphous PVS-derived ceramic after annealing treatment of 50 h at 1350  $^{\circ}$ C. Large scale contrast variations in the elemental maps are caused by thickness variations of the TEM specimen

# 3.2.2 PVS-derived material

According to electron diffraction and electron spectroscopic imaging the microstructure of PVS-derived material is still completely amorphous after annealing 50 h at 1350 °C in nitrogen (Fig. 22). The bright field image and the corresponding elemental maps produced by electron spectroscopic imaging reveal a homogeneous distribution of the elements.

The diffraction patterns show an amorphous ring system which confirmed that the material was fully amorphous. However, the SAD rings show intensity deviations which trace back to the advanced state of ordering in the amorphous 1350 °C product.

If the annealing temperature is raised to 1500 °C crystallization occurs. Elemental distribution images reveal in conformity with the phase diagram (Fig. 4) the existence of SiC and C (Fig. 23). In the bright field image the crystallized matrix can be seen. The elemental



Fig. 23. Bright field image and elemental distribution images of a PVS-derived ceramic after annealing for 50 h at 1500  $^{\circ}\mathrm{C}$  in nitrogen

maps reveal that the microstructure consists of crystalline SiC and of carbon segregations. Compared to the product obtained at 1350  $^{\circ}$ C the nitrogen content is considerably reduced.

In contrast to the PHMS-derived ceramic nitrogen is removed almost completely during the crystallization process. Only small amount of nitrogen can be detected by ESI investigations.

## 4. Creep Behaviour

Typical creep curves of PVS- and PHMS-derived ceramics are shown in Figs. 24 and 25, respectively.

Both materials show similar creep behaviour characterized by a high initial deformation (up to 2%) and extremely low deformation rates at a later stage of creep (e.g.  $1.7 \times 10^{-8}$  s<sup>-1</sup> after 100 h at 1550 °C). However, while the strain rates after 100 h creep deformation are almost the same, e.g.  $1.5 \times 10^{-8}$  and  $2 \times 10^{-8}$  s<sup>-1</sup> at 1550 °C for the PVS- and for the PHMS-derived material, respectively, and reproducible, the difference in total strain between the two materials is higher and the primary creep deformation at the beginning of the experiments varies from specimen to specimen. This leads to the result, that tests at a lower temperature may reveal higher deformation due to an arbitrary higher deformation at the beginning of the creep test as e.g. shown in Fig. 24.

The total strain after  $4 \times 10^5$  s creep deformation at 1550 °C and 100 MPa compression stress is 2.5% for the PHMS-derived material while the deformation of the PVS-derived material is only 1.4%.

# 4.1 Primary creep deformation

It is assumed that a part of the extraordinary initial deformation during compression loading is a stress-independent shrinkage due to the densification of the residual porosity



Fig. 24. Creep curves of the PVS-derived ceramic at 100 MPa compression stress for different temperatures



Fig. 25. Creep curves of the PHMS-derived ceramic at 100 MPa compression stress for different temperatures  $% \left( {{{\rm{C}}_{{\rm{B}}}} \right)$ 

of the material also observed in stress-free dilatometer measurements [15]. Since the maximum processing temperature of the precursor-derived materials attained during pyrolysis is only 1050 °C, it is possible that a sinter shrinkage with a reduction of porosity takes place at the much higher creep testing temperature. Another explanation for the high primary creep deformation could be a shrinkage due to the densification of the amorphous state, also observed during heat treatment of quenched glasses [27].

The higher deformation of the PHMS-derived materials is maybe due to its higher porosity (14%) compared to that of the PVS-derived material (4%). The porosity was determined by optical microscopy and a digital image analysis system.

#### 4.2 Stress dependence of the creep deformation

Assuming power law creep:

$$\dot{\varepsilon} = C\sigma^n \exp\left(-\frac{Q}{RT}\right) t^{-c} \,. \tag{5}$$

The results reveal that the stress exponent n increases with increasing creep stress. E.g. the stress exponent of the PHMS-derived ceramic measured after 100 h creep deformation at 1400 °C increases from n = 0.24 at stresses between 30 and 100 MPa to n = 1.35 between 100 and 200 MPa [28]. A possible explanation for this behaviour is the superposition of a stress dependent and a stress independent deformation mechanism:

$$\dot{\varepsilon} = \dot{\varepsilon}(\sigma, T, t) + \dot{\varepsilon}(T, t) \,. \tag{6}$$

However, further experiments are necessary to explain this phenomenon.

# 4.3 Influence of crystallization on the temperature dependence of the creep rates

# 4.3.1 PHMS-derived material

The creep rate of the PHMS-derived ceramic after 100 h decreases from  $3.2 \times 10^{-8} \text{ s}^{-1}$  at 1500 °C to  $1.7 \times 10^{-8} \text{ s}^{-1}$  at 1550 °C. While the materials are still X-ray amorphous



after the creep tests at 1550 °C, TEM investigations revealed the formation of nanosized crystalline  $Si_3N_4$  and carbon segregations. Parts of the matrix still remained amorphous Si-C-N phase (Fig. 26).

In some regions of the matrix silicon and oxygen as silicon oxide can be detected. Elemental distribution images for silicon, carbon, nitrogen and oxygen of this material show the results very clearly. As can be seen from these images nanosized silicon nitride crystals grow from the amorphous matrix into the silicon oxide rich parts in this sample.

#### 4.3.2 PVS-derived material

The temperature dependence of the strain rates during creep measured after 100 hours creep deformation is unusually low. From the creep curves at 1400 and 1500 °C an activation energy Q of about 250 kJ/mol was calculated for both materials assuming a ther-



Fig. 27. TEM bright field image and elemental distribution images of the material obtained from PVS after a creep test at 1550 °C with 100 MPa compression stress for  $4 \times 10^5$  s in air

mally activated process. At 1550 °C the creep rate of the PVS-derived material is only 7% higher than at 1500 °C, which would give an even lower activation energy of only 27 kJ/mol. The reason for this result may be due to different material states. Whereas after creep tests at 1550 °C the matrix of the PVS-derived material consists mainly of nanosized  $Si_3N_4$  grains and segregations of carbon at the grain boundaries beside some residual amorphous Si-C-N phase and some silicon oxide (Fig. 27) the samples tested at lower temperatures are much less crystalline or even all-amorphous.

Obviously, crystallization of the material at 1550 °C reduces the creep rate at this temperature as compared to that of amorphous material tested at lower temperature. Therefore, comparing the creep curves in the temperature range between 1400 and 1550 °C means dealing with different materials.

#### 4.4 Influence of atmosphere

Owing to the oxygen-containing atmosphere during the creep tests the materials are sealed by a passivating coating made of silicon oxide [29]. As a consequence, the phase formation during these investigations leads to microstructures which still contain an amorphous phase as well as crystalline silicon nitride and carbon segregations. No decomposition reactions by loss of nitrogen according to Eq. (1) as described in the previous chapter is observed because this self-sealing effect provides an effective diffusion barrier that suppresses the loss of nitrogen. Additionally, due to this passivating layer a remarkable oxidation resistance of the materials is observed.

#### 5. Conclusion

The ceramization of the polysilazanes PHMS and PVS at temperatures up to  $1050 \,^{\circ}$ C leads to the formation of amorphous Si–C–N ceramics. The composition of both ceramics is strongly determined by the molecular structure and the composition of the precursor polymer. In the case of the PVS the vinyl groups polymerize in an early stage of the pyrolysis (around 350 °C) yielding in a separation of carbon and in a ceramic which shows finally a higher carbon content compared to PHMS where methyl groups with a reduced reactivity are split off during the condensation process.

With the disappearance of the Si–C bonds combined with the vinyl group polymerization a formation of Si–N bonds takes place resulting finally in tetrahedral configurations of silicon nitride and leaving behind only a small portion of Si tetrahedra "mixed" in C and N if at all. The condensation reaction of PHMS polymer chains on the other side is dominated by the reaction of methyl groups (connected exclusively with Si) among each other or with H (bonded to N or Si or to C resulting from the methyl–methyl reaction) leaving behind finally tetrahedral configurations of silicon carbide, silicon nitride and silicon units with mixed C/N environment as well as trigonal sp<sup>2</sup>-hybridized carbon units of graphite.

Since the types of short-range ordering observed are in accordance with the structural units of the thermodynamically stable (crystalline) phases the system obviously minimizes its free energy during pyrolysis equivalent to the stable phase equilibria of the ternary system Si-C-N indicating that the free energy of the amorphous Si-C-N phase also has minima located in the same composition ranges as that of the crystalline phases. In consequence, during ceramization of PVS the composition approaches the tie line  $Si_3N_4 + C$  and that of PHMS the three-phase field of  $Si_3N_4 + SiC + C$ .

This result gives a simple explanation for the phase separation observed experimentally in as-pyrolyzed PHMS-derived material and in material similar in composition to the PVS-derived material reported elsewhere [30]. Following this explanation consequently one can predict that small angle scattering experiments with PVS-derived material in the as-pyrolyzed stage should also reveal a heterogeneous material consisting of amorphous  $Si_3N_4$  and amorphous C.

As with crystallization of the heterogeneous amorphous materials the stable phases are formed, the ceramization of PHMS and PVS provides a means to build up silicon nitride/carbide-based composite ceramics from the corresponding structural units on an atomic scale. Moreover, certain amounts of carbon can be incorporated into the materials depending on the type of polymer and the composition of the ceramics.

Owing to the different architecture of these ternary Si–C–N ceramics their properties differ. In this connection the electrical conductivity of the PHMS- and PVS-derived ceramics can be seen in Fig. 28.

These measurements provide a sensitive probe for the different structural arrangements and compositions of the two materials. The studies reveal that the PVS-based material which contains a higher amount of sp<sup>2</sup>-hybridized carbon compared to the PHMS-based material also exhibits higher values of the electrical conductivity [13, 16]. It is interesting to note that both ceramics exhibit semiconducting properties.

The results from the preliminary creep studies reveal an interesting potential of creep resistance at temperatures at least as high as 1550 °C since the creep rates after an initial stage of substantial deformation are quite reproducible and become very small (e.g.  $1.5 \times 10^{-8} \text{ s}^{-1}$ ). Even after 100 h of creep the deformation rate was still decreasing indicating that creep still has not approached secondary creep. Furthermore, the creep rates in this stage were quite reproducible although the materials investigated were still poorly developed and e.g. differed substantially in porosity.



Fig. 28. Electrical conductivity of the amorphous silicon carbonitride ceramics obtained by pyrolysis of the polysilazanes PVS and PHMS at 1050  $^\circ\mathrm{C}$ 

The reason for the substantial creep resistance of precursor-derived ceramics is probably due to the lack of grain boundaries and a rather high viscosity, i.e. a very low diffusion coefficient in the predominantly covalent bonded amorphous material.

In the light of this potential of creep resistance it seems to be worthwhile to investigate the initial creep deformation in more detail and to find out whether the extraordinary initial deformation can be decreased by a decrease of porosity.

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