THERMOLYSIS MECHANISMS, AMORPHOUS STATE, AND CRYSTALLIZATION

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ABSTRACT

The transformation of polysilazanes and polysilylcarbodiimides into amorphous Si-C-N ceramics based on solid state NMR, IR and mass spectroscopy studies is described. The ceramization mechanisms and the phase formation during the polymer-ceramic transformation are discussed. Moreover, the structure of the obtained amorphous ceramic solids is derived from X-ray and neutron small angle scattering investigations. The obtained results reveal essential relations between the architecture of the preceramic polymers and the corresponding amorphous stages. Furthermore, TEM is applied for the characterization of the corresponding crystalline solids.

The experimental data are combined with calculations based on the CALPHAD approach in order to provide a quantitative description for the thermochemistry of the polymer systems and for the formation of the ceramic phases that evolve from the precursors.

1. INTRODUCTION

Owing to the outstanding thermomechanical properties of silicon nitride- and carbide-based ceramics [1-3] intensive efforts have been made to establish novel processing routes for the preparation of these materials. One route for the preparation of such ceramics is the powdertechnology approach carried out by liquid phase sintering of silicon nitride and carbide powders in the presence of oxide additives like alumina and yttria [4, 5].

In order to expand the spectrum of the structure and thus of the properties of these ceramics also alternative routes have been developed which deal with the architectural design on an atomic scale. In this connection the precursor route is a main field of research. The objective of this route is to build up novel materials from molecular units. For that purpose polymer precursors are at first synthesized from monomer units and subsequently transformed into ceramics by solid state thermolysis. After the thermally induced transformation of the preceramic polymers amorphous ceramic solids are obtained which can be crystallized into the thermodynamically stable phases by further heat treatment at higher temperatures [6, 7].

For the preparation of silicon nitride/carbide-based composites polysilazanes [8-11] and polysilylcarbodiimide precursors [12-15] have been successfully applied.

However, there is still a lack of information on the relationship of the precursor structure and composition to the phase formation and the structure of the corresponding amorphous and crystalline stages which evolve during heat treatment.

This paper describes the transformation of preceramic compounds into ternary Si-C-N ceramics and summarizes a detailed study presented in [16]. Polysilazanes and polysilylcarbodiimides serve as model compounds. The ceramization process monitored by solid state NMR, IR and mass spectroscopy is described. Moreover, results on the investigation of the obtained amorphous solids observed by X-ray and neutron small angle scattering as well as of the crystalline solids by TEM are included. Finally, a comprehensive

treatment of the thermochemistry of the precursors based on thermodynamic data is reported and combined with the experimentally results in order to provide a quantitative description for the thermally induced ceramization behavior and for the phase formation of Si-C-N ceramic precursors.

2. PRECERAMIC COMPUNDS

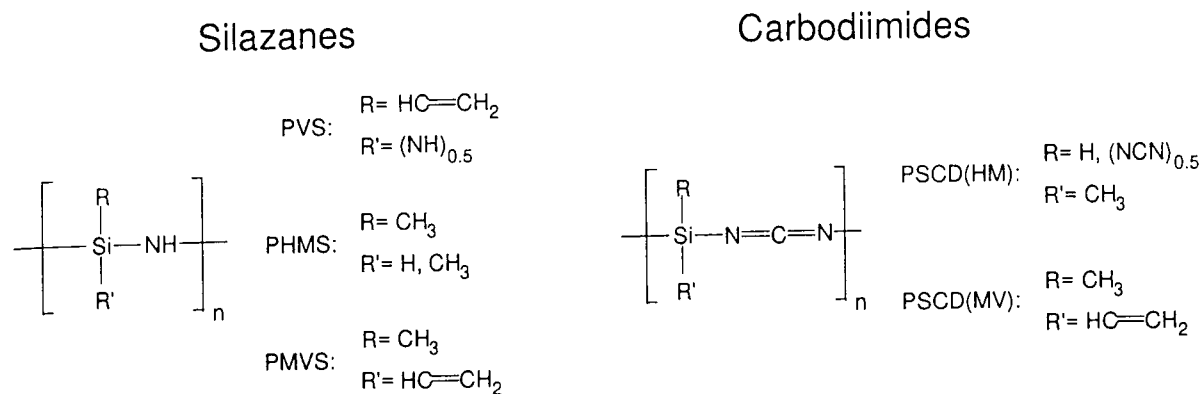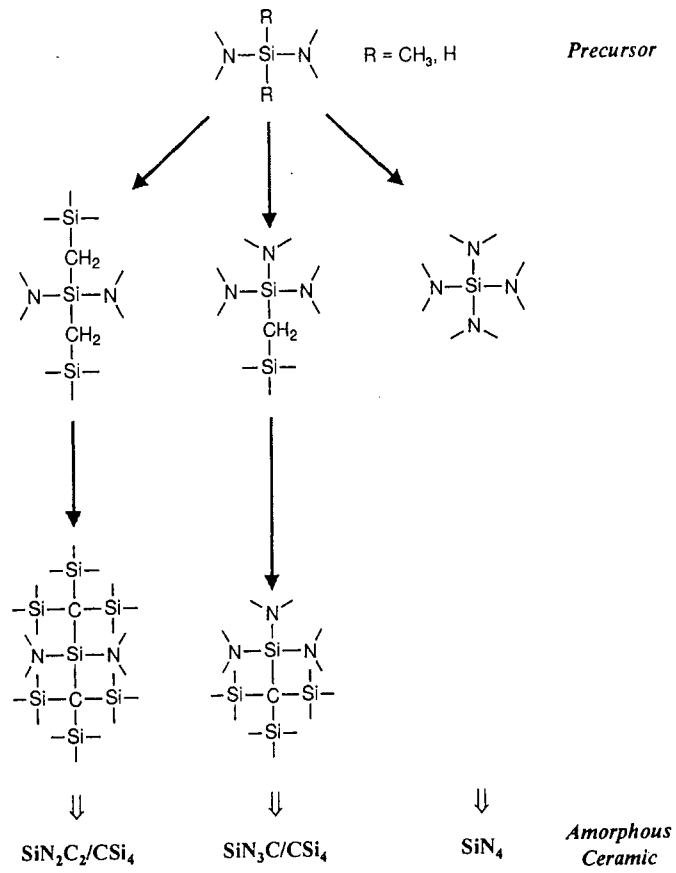The preceramic compounds investigated in this study are summarized in Fig. 1.

Fig. 1 Structural units of the preceramic compounds investigated in this study

In the case of the silazane-based systems Polyvinylsilazane PVS, Polyhydridomethylsilazane PHMS and Polymethylvinylsilazane PMVS are considered. In addition, the carbodiimide-based compounds PSCD(HM) and PSCD(MV) are studied.
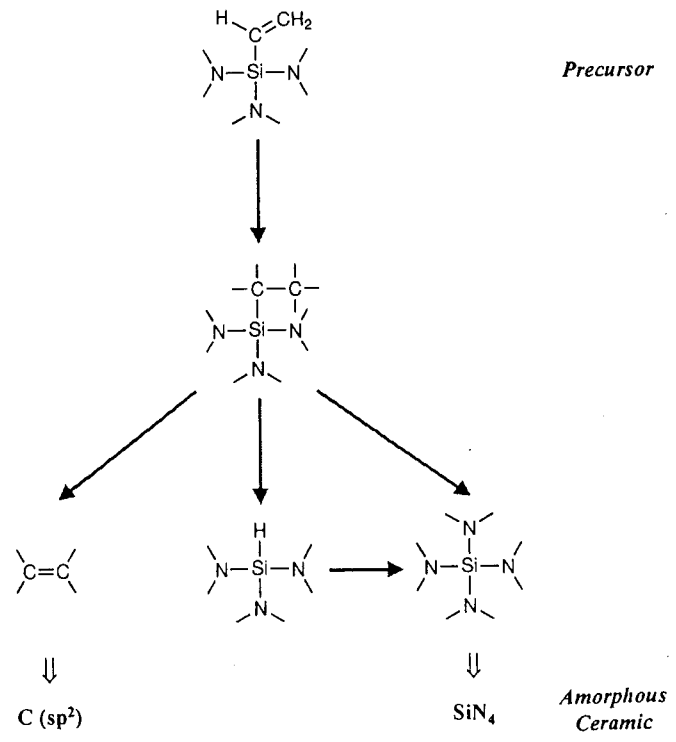
3. THERMOLYSIS AND CERAMIZATION

The evolution of the structural units of the polysilazane precursors into amorphous Si-C-N ceramic solids up to 1050 °C is shown in Fig. 2.

a)

R = CH$_3$, H   *Precursor*

$\Downarrow$ $\Downarrow$ $\Downarrow$

SiN$_2$C$_2$/CSi$_4$ SiN$_3$C/CSi$_4$ SiN$_4$ *Amorphous Ceramic*

b)

Precursor

$\Downarrow$ $\Downarrow$

C (sp^2)   SiN$_4$ *Amorphous Ceramic*

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Precursor
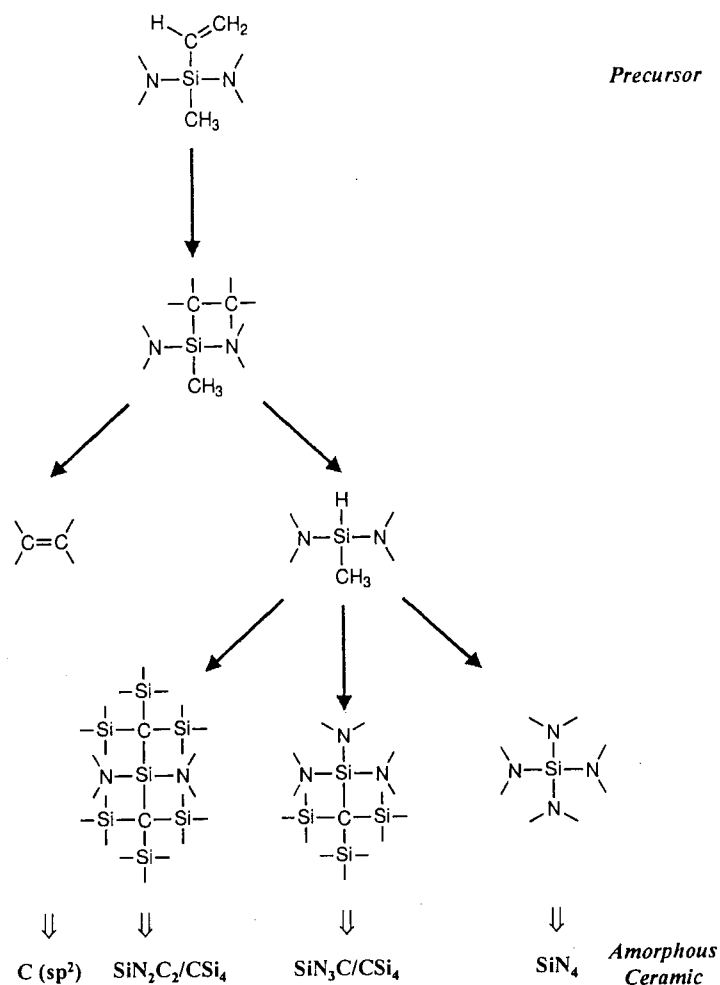
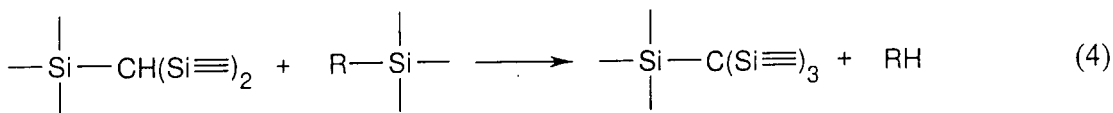C (sp²)   SiN₂C₂/CSi₄   SiN₃C/CSi₄   SiN₄   *Amorphous Ceramic*

Fig. 2 Evolution of structural units during the conversion of the polysilazanes PHMS (a)), PVS (b)), and PMVS (c)) into amorphous Si-C-N ceramics up to a thermolysis temperature of 1050 °C

The investigation of the ceramization by ^{13}C and ^{29}Si solid state NMR, IR as well as mass spectroscopy reveal in the case of the polymer PHMS crosslinking reactions that involve Si-CH$_3$ and Si-H units:

$$-Si-CH_3 + H_3C-Si- \longrightarrow -Si-CH_2-Si- + CH_4 \qquad (1)$$

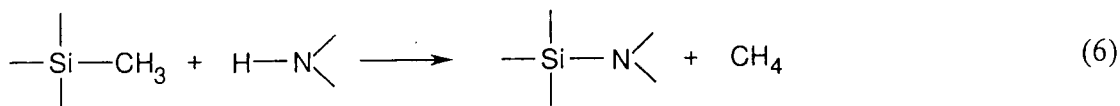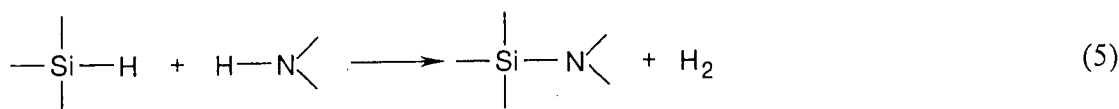$$-Si-CH_3 + H-Si- \longrightarrow -Si-CH_2-Si- + H_2 \qquad (2)$$
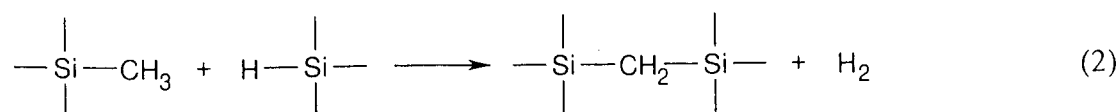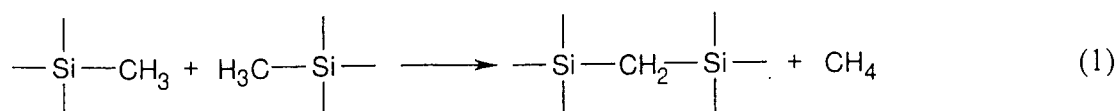
These polycondensation reactions occur at temperatures around 500 °C and are accompanied by the evolution of methane and hydrogen. If the temperature is raised up to 1050 °C these reactions proceed finally resulting in the formation of tetrahedral CSi_4 structural units:
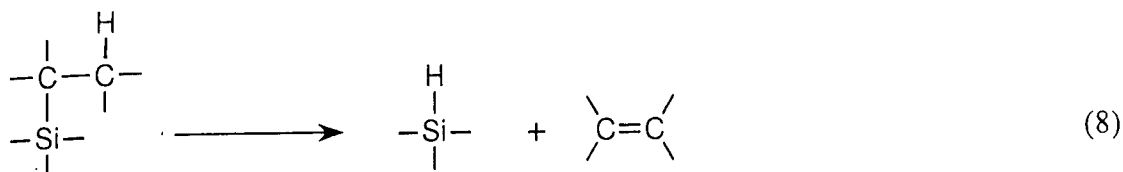
$$-\overset{|}{\underset{|}{Si}}-CH_2-\overset{|}{\underset{|}{Si}}- \ + \ R-\overset{|}{\underset{|}{Si}}- \ \longrightarrow \ -\overset{|}{\underset{|}{Si}}-CH(Si\!\equiv\!)_2 \ + \ RH \qquad (3)$$

$$-\overset{|}{\underset{|}{Si}}-CH(Si\!\equiv\!)_2 \ + \ R-\overset{|}{\underset{|}{Si}}- \ \longrightarrow \ -\overset{|}{\underset{|}{Si}}-C(Si\!\equiv\!)_3 \ + \ RH \qquad (4)$$

$(R=CH_3, H)$

At temperatures above 500 °C Si-N bonds are formed via condensation reactions involving N-H units:

$$-\overset{|}{\underset{|}{Si}}-H \ + \ H-N\!\!\begin{array}{c}\diagup\\\diagdown\end{array} \ \longrightarrow \ -\overset{|}{\underset{|}{Si}}-N\!\!\begin{array}{c}\diagup\\\diagdown\end{array} \ + \ H_2 \qquad (5)$$

$$-\overset{|}{\underset{|}{Si}}-CH_3 \ + \ H-N\!\!\begin{array}{c}\diagup\\\diagdown\end{array} \ \longrightarrow \ -\overset{|}{\underset{|}{Si}}-N\!\!\begin{array}{c}\diagup\\\diagdown\end{array} \ + \ CH_4 \qquad (6)$$
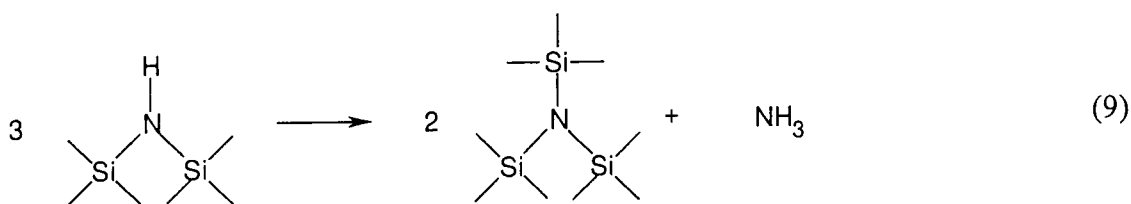
Owing to these reactions the amount of SiN_3C and SiN_4 sites continuously increases at the expense of SiN_2CH and SiN_2C_2 units. Finally, an amorphous covalent solid is obtained at 1050 °C that consists of SiN_4, SiN_3C, SiN_2C_2 as well as of CSi_4 tetrahedrons. In addition the structural units of sp^2-hybridized carbon are present within the amorphous state due to the thermal decomposition of the gaseous by-product methane above 500 °C:

$$CH_4 \rightarrow C_{sp^2} + 2\ H_2 \qquad (7)$$

Thermal treatment of the polymer PVS up to 300 °C induces crosslinking by polymerization of the vinyl groups (Fig. 2b)). If the temperature is further raised cleavage of Si-C bonds via a β-elimination reaction occurs:

$$\begin{array}{c}
\text{H} \\
| \quad | \\
-\text{C}-\text{C}- \\
| \quad | \\
-\text{Si}- \\
|
\end{array}
\quad\longrightarrow\quad
\begin{array}{c}
\text{H} \\
| \\
-\text{Si}- \\
|
\end{array}
\quad+\quad
\begin{array}{c}
\backslash \quad / \\
\text{C}=\text{C} \\
/ \quad \backslash
\end{array}
\qquad (8)$$

Subsequent reaction of the received Si-H units according to equation (5) around 500 °C leads to Si-N bonds. As a result Si-C bonds present in the preceramic polymer are quantitatively transformed into Si-N bonds yielding an amorphous ceramic solid at 1050 °C which is build up by SiN_4 groups. Moreover, significant amounts of ammonia are detected by mass spectroscopy between 200 and 500 °C suggesting a transammination reaction that includes =N-H silazane groups and yields NSi_3 units:

$$3 \quad
\begin{array}{c}
\text{H} \\
| \\
\text{N} \\
/ \quad \backslash \\
\text{Si} \quad \text{Si}
\end{array}
\quad\longrightarrow\quad
2 \quad
\begin{array}{c}
| \\
-\text{Si}- \\
| \\
\text{N} \\
/ \quad \backslash \\
\text{Si} \quad \text{Si}
\end{array}
\quad+\quad NH_3 \qquad (9)$$

Beside these structural units of silicon nitride sp^2-hybridized carbon units formed according to equation (8) are present within the amorphous ceramic state. Moreover, the thermal degradation of the hydrocarbon chains of the crosslinked polymer (Fig. 2b)) leads to the cleavage of C-C bonds and to the evolution of methane which subsequently contributes to the content of solid carbon as described in eq. (7).

The preceramic compound PMVS contains both $Si-CH_3$ and $Si-CH=CH_2$ units (Fig. 1) and can be considered a hybrid of the polymers PHMS and PVS. Therefore, ceramization mechanisms described for these two polymers are observed. As can be seen from Fig. 2c) the reactions mentioned in eq. (1) - (8) occur during ceramization finally resulting in an amorphous ceramic solid made of SiN_xC_y (x = 2-4, x + y = 4) and CSi_4 tetrahedrons as well as of sp^2-hybridized carbon units.

The structural evolution of the precursors PSCD(HM) and PSCD(MV) during the ceramization up to 1050 °C is given in Fig. 3.
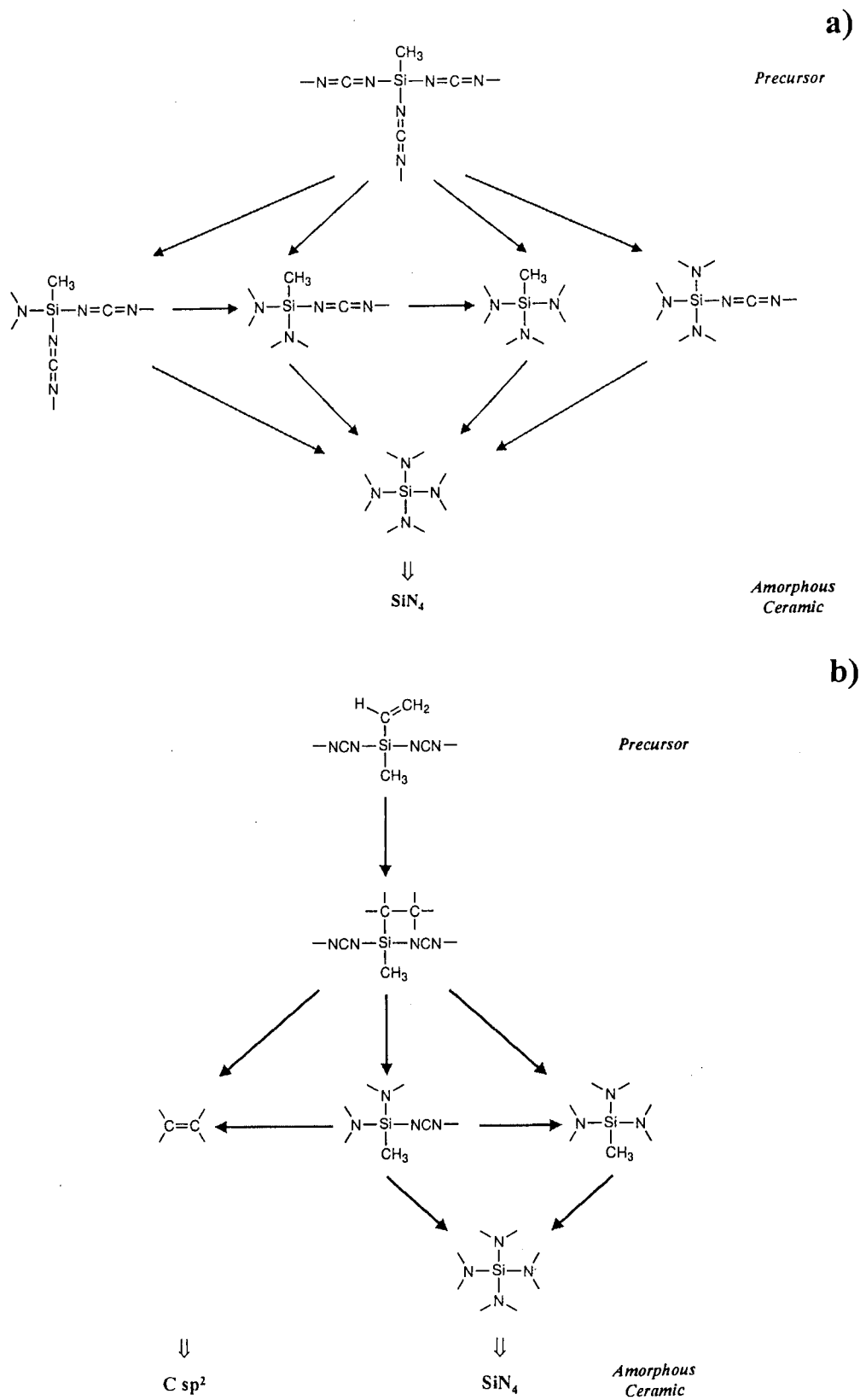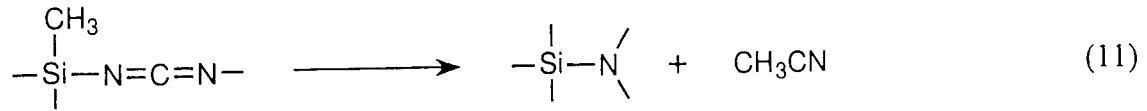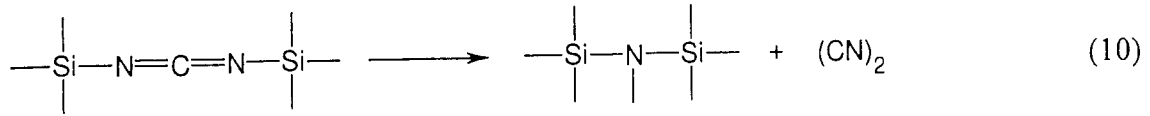
Fig. 3 Evolution of structural units during the conversion of the polysilylcarbodiimides PSCD(HM) (a)) and PSCD(MV) (b)) into amorphous Si-C-N ceramics up to a thermolysis temperature of 1050 °C

In these cases a thermal degradation of the carbodiimde groups into the structural units of silicon nitride occurs, which is accompanied by the evolution of $(CN)_2$ as well as CH_3CN suggesting transformation reactions according to:

$$-\overset{|}{\underset{|}{Si}}-N=C=N-\overset{|}{\underset{|}{Si}}- \quad \longrightarrow \quad -\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{N}}-\overset{|}{\underset{|}{Si}}- \;+\; (CN)_2 \qquad (10)$$

$$-\overset{\overset{\displaystyle CH_3}{|}}{\underset{|}{Si}}-N=C=N- \quad \longrightarrow \quad -\overset{|}{\underset{|}{Si}}-N\overset{/}{\underset{\backslash}{}} \;+\; CH_3CN \qquad (11)$$

As a result SiN_4 tetrahedrons are present within the amorphous ceramic state beside sp^2-hybridized carbon units. These carbon units trace back to the thermal decomposition of the gaseous by-products mentioned in equation (10) and (11) into the elements. Moreover, the transformation reaction (7) of methane that evolves during thermolysis as well as the β elimination (eq. (8)) in the case of PSCD(MV) (Fig. 3b)) serve as further pathways for the incorporation of solid carbon.

4. CHARACTERIZATION OF THE AMORPHOUS CERAMIC SOLIDS BY SMALL ANGLE SCATTERING

In the previous sections the short-range order of the amorphous ceramic solids that evolves during the ceramization of the precursors was described. Based on these results further investigations were carried out to gain an inside into the medium-range order of these materials. For that purpose the PVS-, PHMS-, PSCD(MV)- and PSCD(HM)-derived amorphous Si-C-N ceramics were characterized by X-ray and neutron small angle scattering. The investigation of these materials by SAXS and SANS reveals signals in the small angle scattering regime that clearly exhibit the presence of regions within the amorphous state which differ in atomic density and/or chemical composition from the surrounding matrix. Based on the results described in the previous section which show that the structural units of silicon nitride and carbide as well as of sp^2-hybridized carbon are present in the amorphous state Si_3N_4, SiC and C have to be considered separation phases.

For every of these phases the ratio $(\Delta\eta^x/\Delta\eta^n)^2$ is calculated where $\Delta\eta = \eta_p - \eta_m$ is the difference of the scattering length densities η between the separation phase p and the corresponding matrix m valid for X-ray (x) and neutron (n) diffraction. In order to identify the separated phase these ratios are compared with the experimentally determined ratios of the invariants Q^x/Q^n:

$$\frac{Q^x}{Q^n} = \left(\frac{\Delta\eta^x}{\Delta\eta^n}\right)^2 \qquad (12)$$

The evaluation of the data suggests that silicon nitride segregations are present in the amorphous ceramics. As a result, the as-received ceramics consist of an amorphous silicon nitride separation phase embedded into an amorphous matrix. The Guinier radius of the separation phase obtained from the X-ray small angle scattering data is determined to be in the range between 0.5 and 1 nm.

The composition of the remaining matrix after subtraction of the content of the separated silicon nitride phase is shown in Fig. 4.
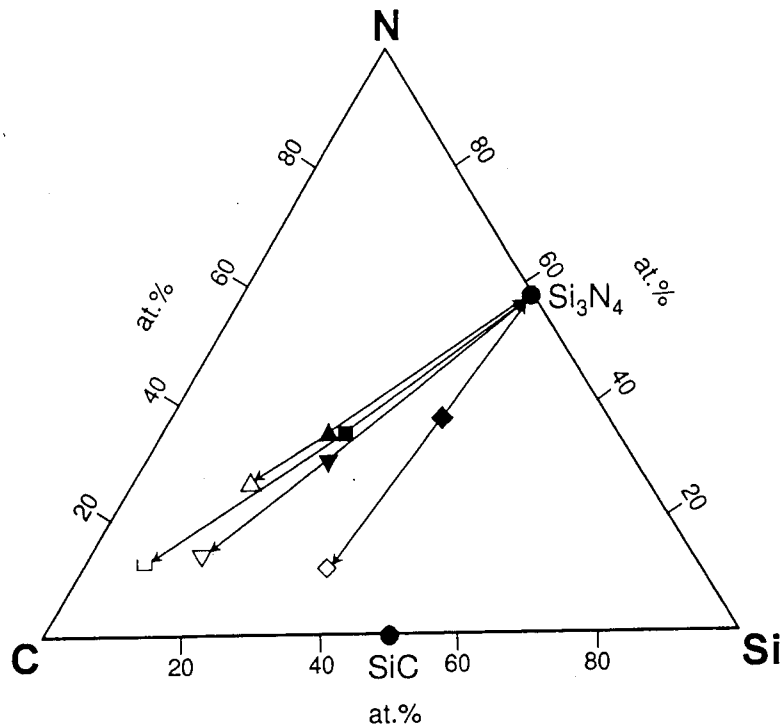

Fig. 4: Si-C-N concentration triangle. The compositions of the PVS- (■), PHMS- (♦), PSCD(MV)- (▼) and PSCD(HM)- (▲) derived ceramics as well as of the corresponding matrix phases (empty symbols) obtained by subtraction of the segregated silicon nitride phase amount are inserted

Owing to the segregation of the silicon nitride phase the matrix compositions of the PVS- PSCD(MV)- and PSCD(HM)-derived ceramics are shifted to the carbon-rich corner of the concentration triangle. These results are in accordance with the observations described in the previous sections which reveal the presence of silicon nitride and sp^2-hybridized carbon structural units. On the contrary the composition of the PHMS-derived matrix phase is transferred to the SiC region of the triangle and enriched in silicon taking into account that the structural units of silicon carbide are also detected in this case (see chapter 3).

Obviously, the thermolysis of the preceramic polymers which initially exhibit a completely homogeneous distribution of the elements induces a phase separation and leads to the segregation of silicon nitride within a carbon- and silicon carbide-enriched matrix phase in the case of the polymers PVS, PSCD(MV), PSCD(HM) and PHMS, respectively. The obtained results also reveal that nano-sized segregations of silicon nitride are preferably formed to silicon carbide.

5. ENERGETIC CONSIDERATIONS

In order to provide a quantitative description of the ceramization behavior and the phase formation of the preceramic polymers discussed so far the CALPHAD approach [17-19] was used to estimate the thermochemistry of these materials. The calculations are based on the compositions of the preceramic compounds determined by chemical analysis. In Fig. 5 these compositions are displayed within the concentration tetrahedron Si-C-H-N.
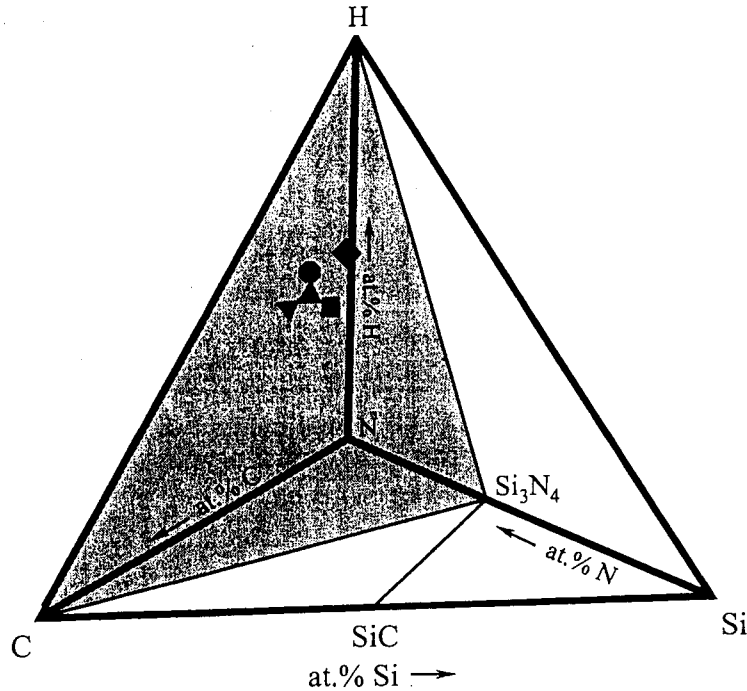

Fig. 5 Si-C-H-N concentration tetrahedron. The compositions of the precursors PVS (■), PHMS (◆), PMVS (●), PSCD(MV) (▼), and PSCD(HM) (▲) are inserted

The polymers investigated can be separated into two classes considering the plane Si_3N_4-C-H that cuts the tetrahedron into two parts. The PVS-, PSCD(HM)- and PSCD(MV)-derived compositions with a ratio [Si]/[N]<0.75 are found inside the subtetrahedron Si_3N_4-C-H-N behind the plane Si_3N_4-C-H. In contrast to that the corresponding compositions related to the polymers PHMS and PMVS (with the ratio [Si]/[N]>0.75) are located in front of the separating plane within the subtetrahedron Si_3N_4-SiC-C-H.

The phase formation in the temperature range between 25 and 1100 °C is illustrated by the phase diagrams shown in Fig. 6, that have been calculated for the experimentally determined polymer compositions.
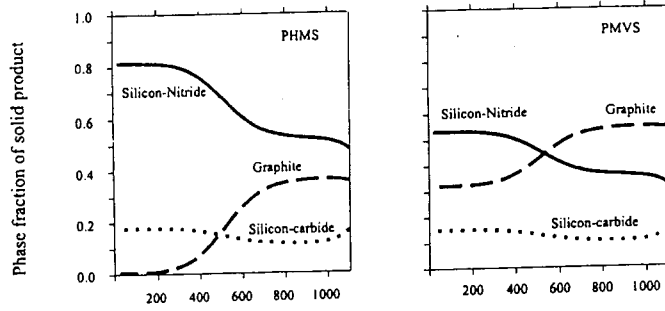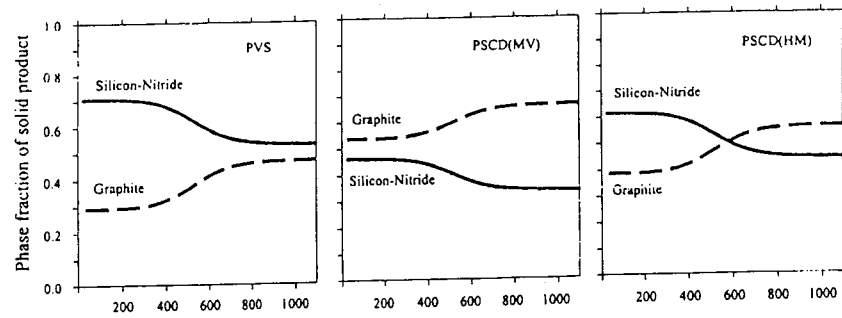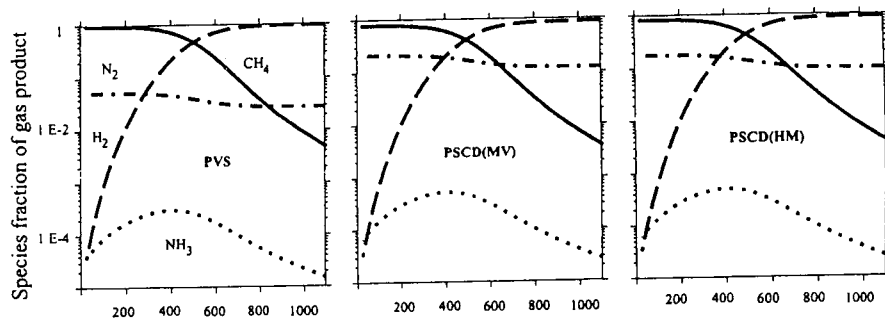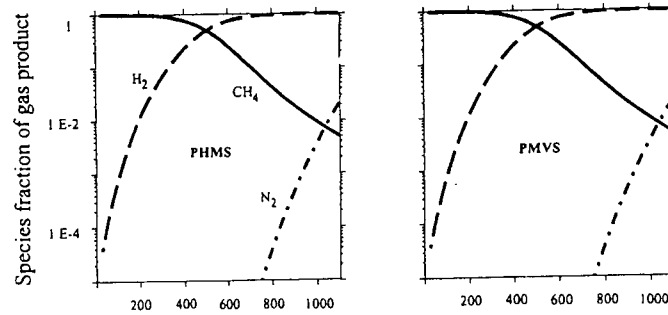
Fig. 6: Results of thermodynamic calculations for polymer-derived compositions given in Fig. 5; a) Phase amounts of the solid product; b) species amounts in gas product

The calculation result is that always both solid and gaseous phases are produced. The appearance of solid phases consisting of the elements Si, C and N and gas phases enriched in hydrogen-containing species appear as a common feature of all polymers investigated. As a consequence the solid phase compositions are located within the basal plane of the concentration tetrahedron which represents the phase equilibria for the ternary system Si-C-N up to 1489 °C. However, there are also essential differences between the two mentioned classes of polymers regarding solid and gaseous phase formation. Polymer compositions located behind the plane Si_3N_4-C-H of the concentration tetrahedron Si-C-H-N (polymers PVS, PSCD(HM) and PSCD(MV)) yield only Si_3N_4 and graphite as solid phases (Fig. 6 a)). In these cases some silicon deficit with respect to the atomic ratio [Si]:[N]=0.75 allows the formation of nitrogen containing gas species (N_2, NH_3) leading to reconcile of the ratio [Si]:[N]=0.75 in the solid product (Fig. 6 b)). If the PHMS- and PMVS-derived compositions are considered some excess silicon with respect to the atomic ratio [Si]:[N]=0.75 is present. In these cases the formation of SiC in addition to Si_3N_4 and carbon (graphite) is observed. The gas phase mainly consists of methane and hydrogen whereas only minor amounts of nitrogen exist at temperatures above ~700°C.

In accordance with the experimental observations discussed in chapter 3 and 4 the above-mentioned thermochemical calculations show that the compositions of the precursor-derived ceramics are located close to the tie line Si_3N_4-C (PVS-, PSCD(HM)- and PSCD(MV)-derived ceramics)and inside the area defined by the three-phase equilibrium Si_3N_4-SiC-C (PHMS- and PMVS-derived ceramics) respectively. The structural investigations of the amorphous ceramics described in the previous sections also reveal that the PVS-, PSCD(HM)-, and PSCD(MV)-derived solids consist of SiN_4 tetrahedra and sp^2-hybridized carbon units. In the case of the PHMS- and PMVS-based materials CSi_4 and SiC_xN_y tetrahedra are present beside SiN_4 and sp^2-hybridized carbon units. In addition, the results on the medium range order (chapter 4) clearly exhibit the presence of silicon nitride segregations. The surrounding matrix is enriched in carbon in the case of the compositions located close to the tie line Si_3N_4-C whereas the amount of silicon is increased if the composition is located inside the triangle Si_3N_4-SiC-C.

These results indicate that the structural units of the thermodynamically stable phases are already preformed within the amorphous states on an atomic and medium range scale. Obviously, the transformation of the polymer systems into the corresponding amorphous ceramics is strongly influenced by the minimization of the Gibbs free energy of these systems. Although kinetic aspects like the formation of metastable radical and gaseous intermediate species play an important part [16] the thermodynamic considerations presented in this chapter provide a quantitative base for the correlation of the polymer composition with the architecture of the corresponding ceramic solids.

6. CRYSTALLIZATION

The crystallization of the amorphous stages depends strongly on the relative stability of the thermodynamic phases. Fig. 7 shows the phase equilibria for the ternary system Si-C-N below and above 1489 °C.
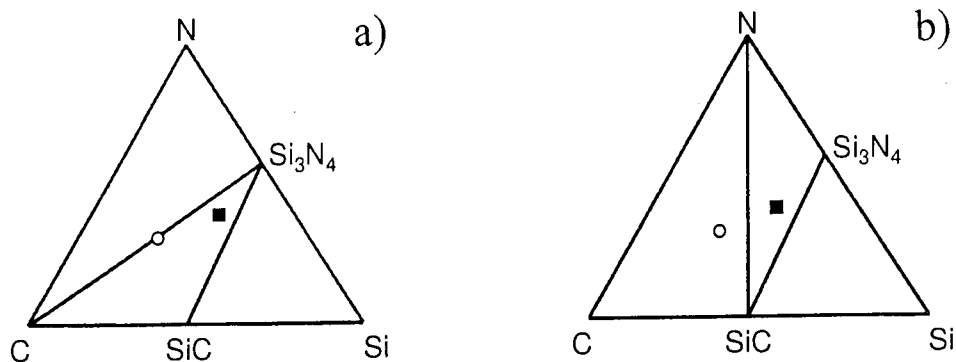
Fig. 7 Phase equilibria of the ternary system Si-C-N below (a)) and above 1489 °C (b)). The compositions of the PHMS- (■) and PVS-derived (o) amorphous ceramic solids are inserted

The compositions of the PHMS- and PVS-derived ceramics are inserted. As can be seen from these diagrams silicon nitride is stable in the presence of carbon below 1489 °C. Above this temperature these two compositions decompose by loss of nitrogen. According to the location of the two ceramics a crystalline silicon nitride/carbide composite material and nitrogen is formed in the case of the PHMS-derived ceramic whereas the PVS-derived material yields a composite consisting of crystalline silicon carbide and carbon as can be shown by transmission electron microscopy [11].

CONCLUSION

The thermally induced transformation of polysilazanes and polysilylcarbodiimides into amorphous ceramic solids has been investigated. At temperatures up to 300°C crosslinking via the polymerization of vinyl groups occurs. If the temperature is further raised the homolytic cleavage of Si-C bonds is observed followed by a β elimination reaction leaving behind Si-H units and sp^2-hybridized carbon. The cleavage of Si-C bonds present in Si-CH$_3$ groups also induces crosslinking reactions that lead to the incorporation of sp^3-hybridized carbide-like units into the amorphous ceramic solid.

Breaking of covalent bonds during the polymer-ceramic conversion is accompanied by the loss of carbon-, hydrogen- and nitrogen-containing gaseous species. Subsequent decomposition of the carbon spezies gives rise to the incorporation of sp^2-hybridized carbon into the amorphous ceramic solids. Bond reformation leads to the evolution of Si-N bonds. As a result the coordination number of silicon with respect to nitrogen increases during the ceramization resulting in SiN$_4$ units. Finally, silicon nitride segregations with a size in the range between 5 and 10 Å embedded into an amorphous ceramic matrix are obtained.

Owing to the polymer-ceramic conversion the solid phase composition is shifted into the Si-C-N plane of the Si-C-H-N concentration tetrahedron. As revealed by a quantitative treatment by the CALPHAD approach this transformation follows the minimization of the Gibbs free energy of the system. In addition the location of the ceramic composition in the Si-C-N phase diagram defines the short range and the medium range order present in the amorphous solids. Ceramics that exhibit a composition close to the tie line Si$_3$N$_4$-C consist of silicon nitride and a matrix phase based on sp^2-hybridized carbon. On the contrary, the matrix phase of compositions that are defined by the three-phase equilibrium Si$_3$N$_4$-SiC-C also contains the structural units of silicon carbide.

Further increase of the annealing temperature results in the transformation of the amorphous into crystalline states which is accompanied by an additional decrease of the Gibbs free energy and the formation of the thermodynamically stable phases.

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