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Characterization of pyrolysed silacyclobutasilazane

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Silacyclobutasilazane (SCBZ) is a candidate organosilicon polymer suited to many high-temperature applications. Pyrolysis of SCBZ occurs over two distinct temperature ranges: 400–800 and 1400–1800 °C. X-ray diffraction analysis showed that amorphous SCBZ transforms to crystalline SiC above 1400 °C. Thin foils of the pyrolysed (1800 °C) SCBZ were prepared and examined using the analytical electron microscope. The material was found to contain ~ 200 nm β-SiC particles scattered through a matrix consisting of ~ 50 nm radiating clusters of pyrolytic graphite crystals and a highly carbonaceous amorphous background. It is suggested that during 1400–1800 °C pyrolysis two major reactions occurred. Initially, SCBZ through nitrogen loss, decomposed to crystalline SiC and amorphous carbon. Subsequent graphitization then produced the radiating crystal clusters.

1. Introduction

Organosilicon precursors have been successfully utilized to produce SiC, Si_3N_4 powders, fibres and thin films, etc. [1–13]. Several advantages of the preceramic polymer route to ceramics compared to inorganic synthetic routes are: (i) energy savings because of low-temperature production capability, (ii) production of extremely pure material, (iii) ease of complex shape fabrication, (iv) production of ceramics and ceramic composites of novel composition. These polymers have been found to be effective as (a) non-fugitive binders for pressureless sintering, and (b) binders as well as carrier for injection-moulding applications [14]. In this paper the transition phenomena of SCBZ to ceramic (SiC) material will be discussed. SCBZ has Si–N–Si in its backbone and large amounts of excess carbon. Results from temperature and chemistry-dependent amorphous to crystalline transformation studies, as well as X-ray diffraction (XRD) and microstructural analyses of the pyrolysed SCBZ materials will be discussed.

2. Experimental procedure

The $[(C_3H_6SiNH)_{0.5}(Ph_2SiNH)_{0.25}(PhSi(NH)_{3/2})_{0.25}]$ preceramic polymer was prepared at Dow Corning via ammonolysis of a mixture of 1,1-dichloro-1-silacyclobutane, diphenyldichlorosilanes and phenyltrichlorosilanes at $\leqslant 20\,°C$. The elemental compositions of the as-formed SCBZ and argon-pyrolysed (1200 °C) SCBZ polymer are given in Table I.

TABLE I Chemical composition of SCBZ

	As-formed (wt %)	1200 °C char (wt %)
C	60.0	48.1
H	6.7	–
N	12.5	15.9
O	–	0.2
Si	21.9	37.6
Total	100.1	101.8

A preweighed amount of gummy and tacky SCBZ polymer was transferred to an alumina boat. The boat was placed in a Lindberg tube furnace where it was heated at the rate of 2 °C min^{-1} to 400 °C and soaked at that temperature for several hours in flowing argon. The polymer thus cured was reweighed. The per cent weight loss was measured after curing. Thermogravimetric analysis (TGA) of the cured polymer was performed between room temperature and 800 °C under flowing high purity (HP) argon for a fixed heating rate of 10 °C min^{-1} using a DuPont thermogravimetric analyser interfaced with an Omnitherm control unit.

Cured polymer was pyrolysed in a graphite resistance-heated Astro furnace by heating at the rate of 10 °C min^{-1} to different temperatures, i.e. 1000, 1400, 1600, 1800 °C. At each final temperature the polymer was soaked for 2 h and subsequently furnace cooled. The entire pyrolysis was carried out under flowing HP argon. Per cent weight reduction was determined as a function of peak temperature. The pyrolysed polymer was black and fragile. Elemental analysis for carbon, hydrogen and nitrogen was performed on the pyrolysed polymer using a Control Equipment Corporation 240-XA elemental analyser. Pyrolysed polymer was finely ground with a boron carbide mortar and pestle. The XRD was performed on the powder using CuK_α radiation and a Philips (NORELCO) wide-range goniometer. An aluminium/tungsten specimen holder [15] was used to aid semiquantitative phase analysis.

Initial attempts to prepare thin foils of pyrolysed polymer (ceramic) were hampered by the highly porous nature of the as-received specimen which crumbled into pieces during early steps in the sample processing. Refinement of techniques and somewhat more durable samples finally permitted this difficulty to be overcome. The most satisfactory preparation of the ceramic samples involved, first, impregnation of the sample in Epotek 353 epoxy resin from which a thin slice was then cut with a diamond-impregnated saw blade. This slice was then cut into a 3 mm diameter wafer and ground to near perforation in the centre by successively finer grits of diamond powder on a VCR Group dimple polisher. This preparation was then transferred to an Edwards IBT 200 ion thinner for final thinning to perforation. Thinning in this instrument was achieved after 8–10 h, using constant rotation with an argon gas flow at about 3 kV. Initially thinned at about 28° simultaneously on both sides, the angle was decreased to 10° as thinning was observed optically to be nearly complete.

The preparation, thinned to perforation in the centre, was then transferred to a Gatan low-background specimen holder for examination in the Jeol 2000 FX analytical electron microscope. The instrument, equipped with light and heavy element Tracor Northern energy dispersive detectors and Tracor Northern 5500 automation system, as well as scanning transmission (STEM) and microbeam electron diffraction capabilities, was found to be well suited for the current investigation.

The instrument was operated at 200 kV with a lanthanum hexaboride (LaB_6) electron source. For electron diffraction, the camera distance was calibrated with an aluminium standard at 100 cm. It was found necessary to use microbeam electron diffraction (MBED) techniques rather than the more conventional selected-area diffraction (SAD) in order to restrict satisfactorily beam interaction with the sample in the area of very small 50–200 nm clusters which comprised a significant portion of the ceramic matrix. Optical and scanning electron microscopic examination was also performed on the thin foils.

3. Results and discussion

3.1. Pyrolysis and chemistry

The SCBZ polymer underwent a weight loss of about 2% during curing. This weight loss is believed to be due to the removal of retained solvent introduced during polymer synthesis. Further reduction in polymer weight has been recorded as a function of temperature between 400 and 1800 °C. TGA data obtained for the temperature range between 400 and 800 °C is shown in Fig. 1. The data reflects that the weight loss of the cured SCBZ begins at around 400 °C and proceeds rapidly up to about 600 °C. The weight-loss rate slows significantly above 600 °C and is essentially negligible at around 800 °C. The loss of weight of the polymer in this temperature range is about 25%, based on the original weight of the cured polymer. This weight loss is related to the loss of low molecular weight oligomers, NH_3 and alkyl groups via decomposition (called "primary pyrolysis") of the polymer.

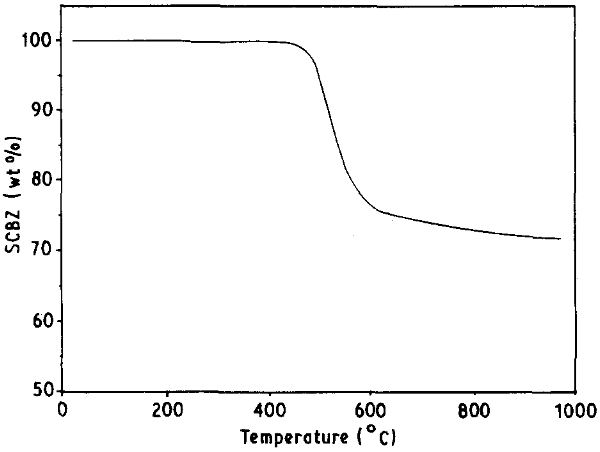

Figure 1 TGA of cured SCBZ: 15.7330 mg, 10 °C min^{-1}, helium.

The weight-loss characteristic above 1000 °C is presented in Fig. 2. Comparing the data plotted in Figs 1 and 2 reveals that SCBZ is thermally weight stable between 800 and 1400 °C. Above 1400 °C the polymer undergoes further weight reduction due to "secondary pyrolysis" until 1800 °C. The elemental (C, H, N) analyses of the pyrolysed polymer are presented in Table II. The data suggest that secondary pyrolysis of the SCBZ polymer occurs via nitrogen loss. Nitrogen loss continues until a stable char is obtained at around 1800 °C.

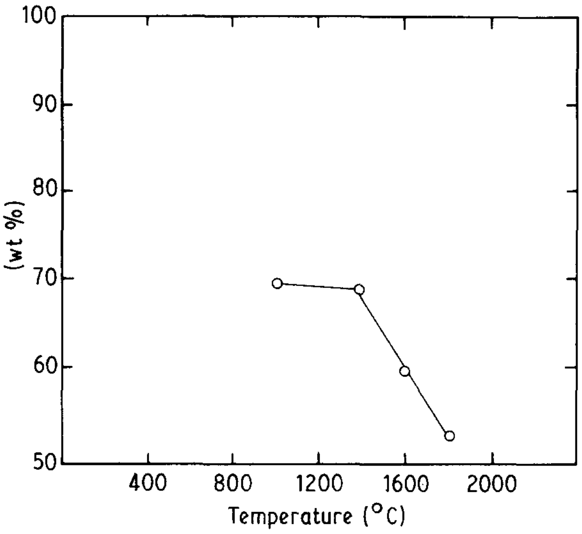

Figure 2 Per cent weight retention of SCBZ versus pyrolysis temperature: 10 °C min^{-1}, soaked at temperature for 2 h in flowing argon.

TABLE II Weight per cent nitrogen as a function of pyrolysis temperature; polymer: SCBZ

Pyrolysis temperature (°C)	C	H	N	Remainder
1400	48.7	0.02	16.72	34.5
1600	52.56	0.28	10.01	36.8
1800	58.40	0.02	0.22	41.4

3.2. Phase analysis

XRD data of the as-pyrolysed and ground char at different temperatures presented in Fig. 3, shows that at pyrolysis temperatures between 1000 and 1400 °C the char residues are amorphous as characterized by a broad hump at $2\theta \approx 20^\circ$ and no SiC-related X-ray peaks. At pyrolysis temperatures of 1600 °C the SiC (β-SiC) materials begin to crystallize as evinced by the appearance of a minor peak at $2\theta \approx 36^\circ$ (1 1 1) with virtually no major loss of amorphous character of the materials. At 1800 °C substantial crystallization of β-SiC has occurred (peaks at $2\theta \approx 36^\circ$ and 60°) with very minor residual amorphous phase.

Although no peak associated with graphitic carbon was identified by XRD analysis of 1800 °C char material, electron diffraction and microchemical analysis confirmed the presence of graphite as will be discussed later. Chemical analyses shown in Tables I and II also confirm the presence of free carbon.

3.3. Microstructure of SCBZ polymer ceramic (7737-51-3) (pyrolysed at 1800 °C in argon)

Optical and scanning electron microscopy at low magnifications (Fig. 4) showed numerous voids/pores up to 100 μm diameter. Lenticular cracks were often associated with these pores and also occurred as narrow medial fractures in otherwise dense zones. The cracks were often 200 μm wide and 500–1000 μm long. These cracks may be the result of tensile stresses during cooling of the ceramic as a consequence of crystallization.

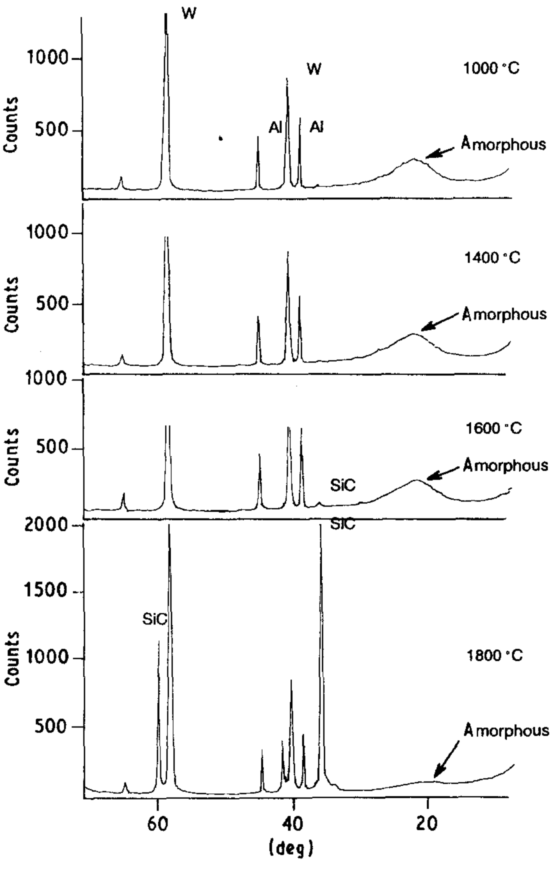

Figure 3 X-ray diffractograms of SCBZ pyrolysed at different temperatures.

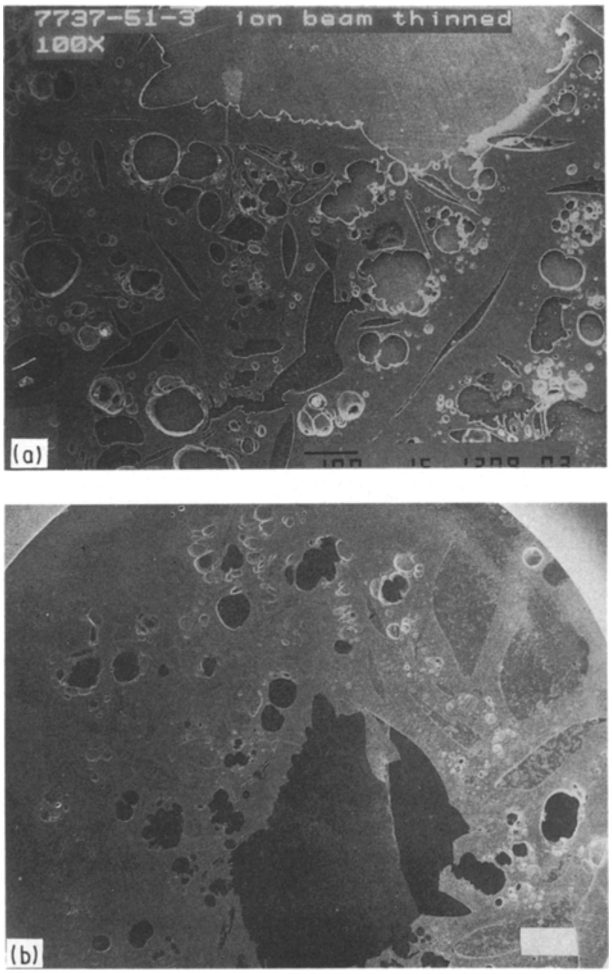

Figure 4 Microstructure of ion-beam thinned foil using the SEM.

Edges of the central ion-thinned perforation in this preparation were sufficiently thin to permit examination in the AEM. Nominal thickness was measured at about 300 nm using the contamination spot technique. The ion-thinned surface was notably irregular on both sides as a consequence of different response to thinning by different exposed constituents.

The thin foil adjacent to the perforation typically showed irregular rounded SiC crystals up to about 250 nm diameter (Fig. 5). Many of these, depending upon their orientation, showed probable bands or lines of diffraction contrast. One example of a series of MBED patterns obtained from many of these discrete crystals is shown in Fig. 6. Although it was not possible on the basis of this work to distinguish the polytypes of SiC, XRD analysis indicated that the crystals were predominantly cubic in structure.

The matrix, at comparatively low magnifications, appeared fairly dense. However, at higher magnifications, spherulitic growths of ~ 50 nm diameter were readily evident as they appeared scattered throughout the otherwise amorphous matrix (Fig. 7). Typically occurring as radiating rosettes, the spherulitic structures in this SCBZ ceramic often exhibited central dark nodes and cross bands of diffraction contrast along the length of the radiating laths.

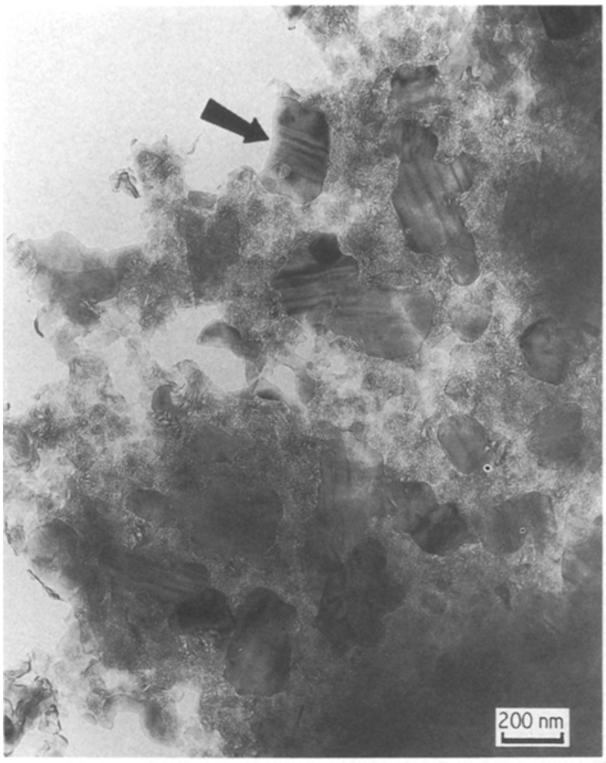

Figure 5 Irregular rounded SiC crystals (arrowed) within pyrolysed SCBZ at the edge of an ion-thinned perforation.

Figure 7 Graphite spherulites (arrowed) surrounding SiC crystals.

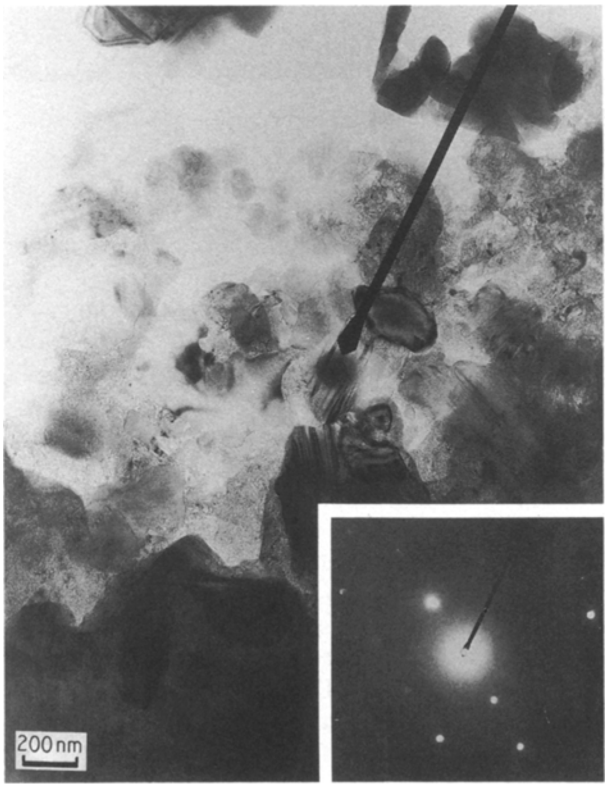

Figure 6 SiC crystals (arrowed) and the typical single-crystal MBED patterns derived from them

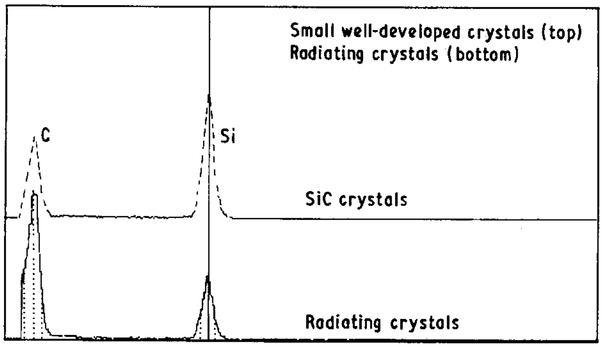

Figure 8 Ultrathin window energy dispersive X-ray spectra comparing carbon and silicon content in SiC crystals (top spectrum) and a spherulitic crystal. Accelerating voltage 200 kV, beam current 136 μA, spot size 3L, condenser aperture 20 μm, 30 tilt in Gatan holder.

Microanalysis of several spherulites was conducted in the AEM using the ultrathin window energy dispersive X-ray spectrometer. The analysis area, being about 100 nm diameter in these foils did not allow spectra to be obtained solely from an individual spherulite. However, the resulting spectra (Fig. 8) showed a high carbon content, substantially higher than that in SiC. The detection of silicon was attributed to contribution of silicon from the carbon-rich siliceous matrix in the analysis area surrounding the spherulites.

A series of MBED patterns was obtained from numerous spherulites. Ring patterns with superimposed single-crystal reflections were commonly recorded, as shown in Fig. 9. From this the spherulites were identified as graphite. This conclusion was also consistent with results of microanalyses described earlier

The matrix surrounding the spherulites showed a characteristic "dappled" structureless morphology and dim, diffuse electron diffraction rings of an amorphous material. Microanalysis with the light element detector revealed a high carbon content and

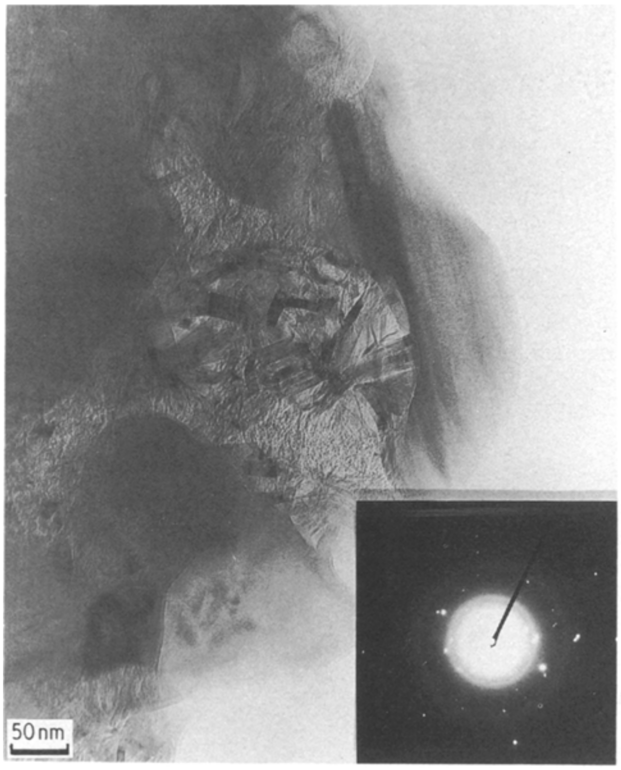

Figure 9 Cluster of radiating pyrolytic graphite (centre) and MBED pattern (inset).

Figure 11 Large graphite laths in the pyrolysed SCBZ.

significant silicon. Locally high concentrations of oxygen were detected (Fig. 10) although correlation of this anomalous oxygen content with a characteristic morphology was not attempted in this study. Well-developed large lath-like structures were also found in some widely scattered portions of the ceramic (Fig. 11). These showed only carbon in the energy dispersive microanalysis spectrum.

High-resolution microanalytical techniques have provided an effective method for characterization of polymer-derived ceramic microstructure. This work revealed the microchemistry, phase characteristics, crystal structure and grain morphology of the SCBZ char consisting of SiC and a large excess of carbon. An extension of this work will be to investigate polymer derived SiC and carbon grains as these interact with SiC particles added as powders.

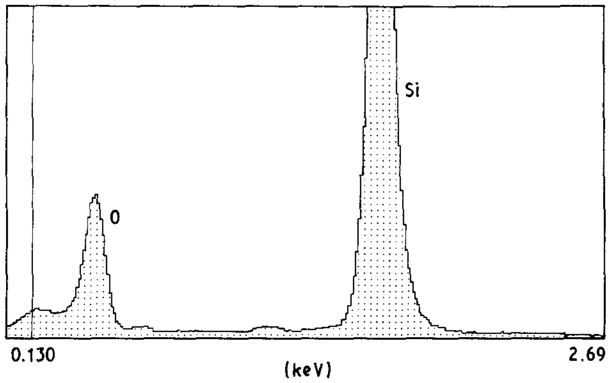

Figure 10 Ultrathin window energy dispersive microanalysis of a local area of unusually high oxygen impurity in SCBZ. Accelerating voltage 200 kV, beam current 113 μA.

4. Summary

1. In a flowing argon atmosphere, SCBZ undergoes "primary pyrolysis" between 400 and 800 °C and "secondary pyrolysis" between 1400 and 1800 °C. Each decomposition process is associated with a weight reduction via loss of volatiles.

2. Primary pyrolysed SCBZ is amorphous and consists essentially of carbon, silicon and nitrogen.

3. Secondary pyrolysed SCBZ consists of fine β-SiC crystals, graphite of spherulitic morphology and some amorphous carbonaceous matrix material.

4. Crystallization of SCBZ initiates at around 1600 °C and proceeds nearly to completion above 1800 °C.

5. Crystallization of the amorphous N–Si–C system occurs via the following reaction:

$$\text{N–Si–C} \rightarrow \text{SiC} + \text{C (graphite)} + N_2\uparrow$$

6. The higher the amount of nitrogen retention in the N–Si–C system, the lower is the crystallinity.

Acknowledgements

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