

Thermal decomposition of carbon-rich polymer-derived silicon carbonitrides leading to ceramics with high specific surface area and tunable micro- and mesoporosity

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Abstract

Herein we report on the thermal decomposition of SiCN polymer-derived ceramics leading to materials with high specific surface area and defined pore sizes. The ceramics were obtained by means of pyrolysis of a carbon-rich poly(diphenylsilylcarbodiimide) precursor and by varying the thermolysis parameters, namely temperature, annealing time and using additional annealing steps. The thermal decomposition of SiCN ceramics is correlated with the carbothermal reaction of amorphous silicon nitride phase with excess carbon and this detrimental event leads to high specific surface area up to $568 \text{ m}^2 \text{ g}^{-1}$ and micro- and mesopores formation in these materials. High-resolution TEM investigations have confirmed that the pores are embedded only in the carbon phase. Moreover, the relationship between the pore sizes and the organization of free carbon phase is discussed.

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1. Introduction

Enhanced control over the specific surface area (SSA) and geometry of pore space in inorganic materials is of great technological interest owing to applications like molecular separation, catalysis and storage. Recent research has made inroads into this issue, devising experimental strategies towards tunable porosity in materials.^{1,2}

However, the increasingly stringent application requirements, such as in high-temperature membrane reactors and molecular separation systems, continuously demand the development of novel porous and multifunctional materials. Silicon-based non-oxide ceramics, such as silicon carbide (SiC), silicon nitride (Si₃N₄) and silicon carbonitrides (SiCN) have increasingly attracted particular attention due to their exceptionally high stability and resistance towards crystallization

and degradation.^{3–5} Microporous SiBCN ceramics have recently shown promising applications in H₂/CO selectivity⁶ and as a protective coating for SnO₂-based gas sensors in harsh reducing environments.⁷ For polymer-derived silicon carbonitride (SiCN) ceramics fabricated by conventional thermolysis routes, demanding techniques such as templating, block-copolymerization and leaching are required to make them mesoporous.^{8–10} An easy template-free method to produce polymer-derived SiCN ceramics with a high degree of porosity has not yet been developed. As the solid-state structure of polymer-derived ceramics (PDCs) is highly sensitive to the molecular structure of the precursor, pyrolysis temperature, annealing time and gas atmosphere during the polymer-ceramic transformation and decomposition, the variation of these parameters enables to tune the porosity in PDCs.

Applications like catalyst support at high temperatures cannot be realized by porous materials like zeolites, silica or alumina which decompose above 1000 °C since they lose their high SSA if they are used for example for methane pyrolysis.¹¹ Generally, systems which develop a microporosity

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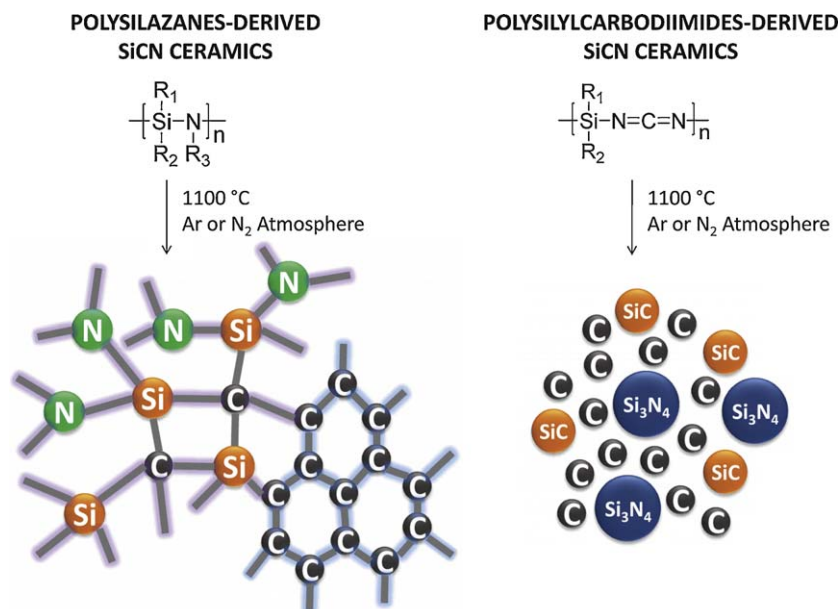


Fig. 1. Comparison between the microstructure of amorphous SiCN ceramics derived from polysilazanes (left) and polysilylcarbodiimides (right) at 1100 °C.

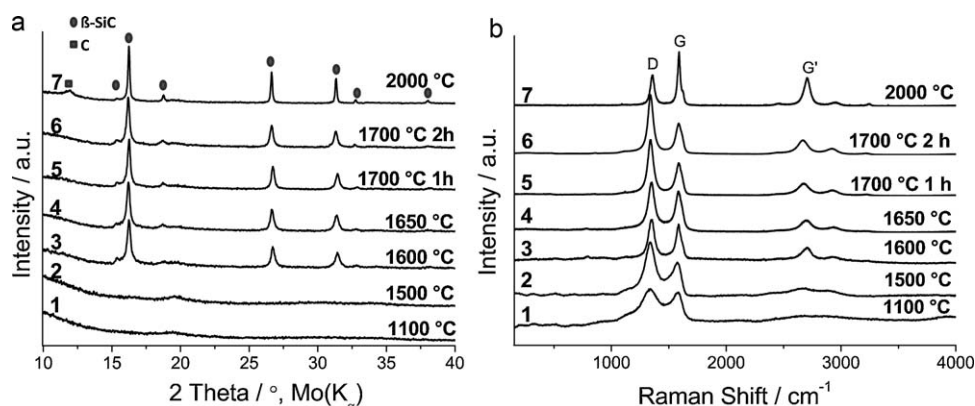


Fig. 2. (a) XRD pattern of samples 1–7 (left); (b) Micro-Raman characterization of samples 1–7.

rarely retain their high SSA up to temperatures as high as 1500 °C.¹¹ Moreover, micropores in carbon materials close in the temperature range between 800 and 1400 °C.¹¹ Therefore, ceramics made from polymers are expected to be suitable porous materials for high temperature applications.

In 1989, Fox et al.¹² patented the formation of high-surface area ceramics made from organosilane by means of sol–gel polymerization of different RSi(OCH₃)₃ in basic and acid medium. The authors observed that the ceramics synthesized from phenyl-containing polysiloxanes (when R = Ph in the trimethoxysilane) developed a high-surface area and microporosity.¹² The specific surface area seems to depend on the organic substituents of the precursors and on the synthesis condition. Moreover, the specific surface area increases with an increase in the SiC content in the ceramic. The same observation was made by Liu et al. in 1995 in the case of pure xerogel synthesized from phenyltrimethoxysilane and pyrolyzed between 1400 and 1500 °C.¹³ In this case, a surface area of 400–500 m² g⁻¹ was obtained. The SSA was observed to increase with an increase

in particle size of crystalline SiC and with annealing time.¹³ In 1994, Reid et al. reported nano- and mesoporous ceramics with high specific surface area up to 170 m² g⁻¹ and a pore volume of 0.12 cm³ g⁻¹ for polycarbosilastirene derived ceramics at 1550 °C. They attributed the properties of the ceramics to their starting composition. The correlation between the SiC crystallite size and the specific surface area was also commented.¹⁴ The intrinsic porosity of ceramics is dependent on the class of precursors used for thermolysis. Therefore, significant differences can be observed by changing the preceramic polymer chemistry.

There are two important classes of polymers as precursors for silicon carbonitride (SiCN) ceramics, namely polysilazanes $-\left[R^1 R^2 \text{Si}-\text{NR}^3 \right]_n-$ and polysilylcarbodiimides $-\left[R^1 R^2 \text{Si}-\text{N}=\text{C}=\text{N} \right]_n-$, where R¹, R² and R³ are organic groups such as methyl, phenyl, etc. (Fig. 1).^{3–5} By the thermal decomposition of polysilazanes at approx. 1100 °C, one single phase amorphous SiCN ceramic can be obtained (Fig. 1, left). As demonstrated by means of solid-state MAS NMR, the polysilazane-derived ceramics contain mixed bonds where

Table 1
Preparation, chemical composition, specific surface area, porosity and SiC crystallite sizes of the samples 1–7 (for the preparation conditions, in the case of the samples 3–5, the sign plus (+) indicates that 2 annealing steps have been used as described in the experimental part).

Sample	Preparation conditions		Si (wt%) ^a	C (wt%)	N (wt%)	O (wt%)	SSA (m ² g ⁻¹)	Micro-pore vol. (cm ³ g ⁻¹) ^b	Micro-/mesoporosity	SiC crystallite size (nm) ^c
	Temp. (°C)	Dwelling time (h)								
1	1100	2	21.80	60.90	16.70	0.60	<1	-	Nonporous	0
2	1500	2	24.05	60.19	15.47	0.29	3	-	Nonporous	0
3	1500 + 1600	2 + 0.5	30.42	62.07	5.99	1.52	440	0.18	Mainly microporous	20–100
4	1500 + 1650	2 + 0.5	32.54	64.25	1.93	1.28	568	0.22	Mainly microporous	20–100
5	1500 + 1700	2 + 1	31.03	66.93	0.67	1.37	513	0.20	Mainly microporous	20–100
6	1700	2	22.69	76.92	0.35	0.04	337	0.07	Meso-/microporous	20–100
7	2000	2	24.06	75.66	0.28	0.00	28	-	Nonporous	50–150

^a Calculated as difference of the other elements.

^b *t*-Method.¹¹

^c TEM.

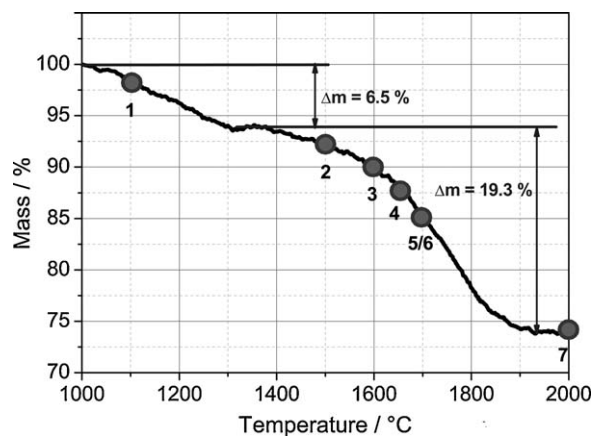


Fig. 3. Relative weight change of pre-pyrolyzed poly(diphenylsilylcarbodiimide) at 1100 °C as determined by high temperature thermogravimetry (HT TG) performed in He up to 2000 °C.

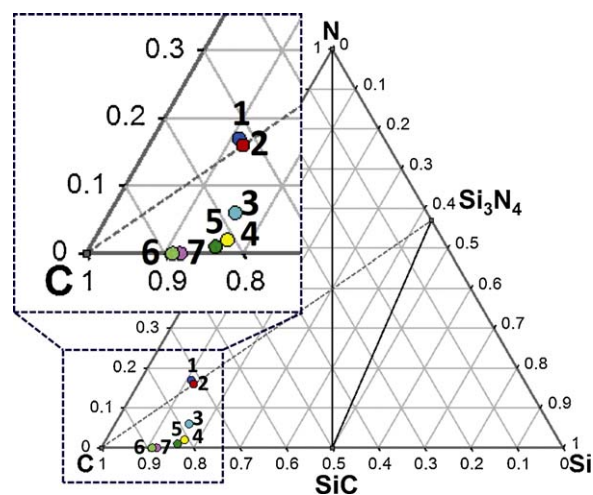


Fig. 4. The elemental composition diagram of the samples 1–7 (as described in Table 1).

silicon is bonded to nitrogen and to carbon at the same time.^{3–5} The SiCN ceramic obtained by the thermolysis of polysilylcarbodiimides at approx. 1100 °C consists of three types of nanodomains (1–3 nm in size) of amorphous silicon nitride (α -Si₃N₄), amorphous silicon carbide (α -SiC) and amorphous carbon (α -C) up to 1450 °C as confirmed by SAXS and MAS NMR (Fig. 1, right).^{3–5,15,16} In this case, no mixed bonds are present in the structure. The differences in the enthalpy of formation reported for the SiCN ceramics obtained from polysilazanes and polysilylcarbodiimides indicate once more that the bonding situation (mixed and non-mixed bonds) plays a significant role with respect to the stability of these systems.^{17,18}

Another important factor which can influence the properties of these materials is the carbon content. Polymer-derived ceramics can incorporate a large amount of free carbon in the microstructure.^{3–5} As already reported, the fine distributed excess of carbon in polymer-derived ceramics can be advantageous for the resistance against crystallization up to high temperatures and, at the same time, generates a complex microstructure for carbon-rich ceramics.¹⁵

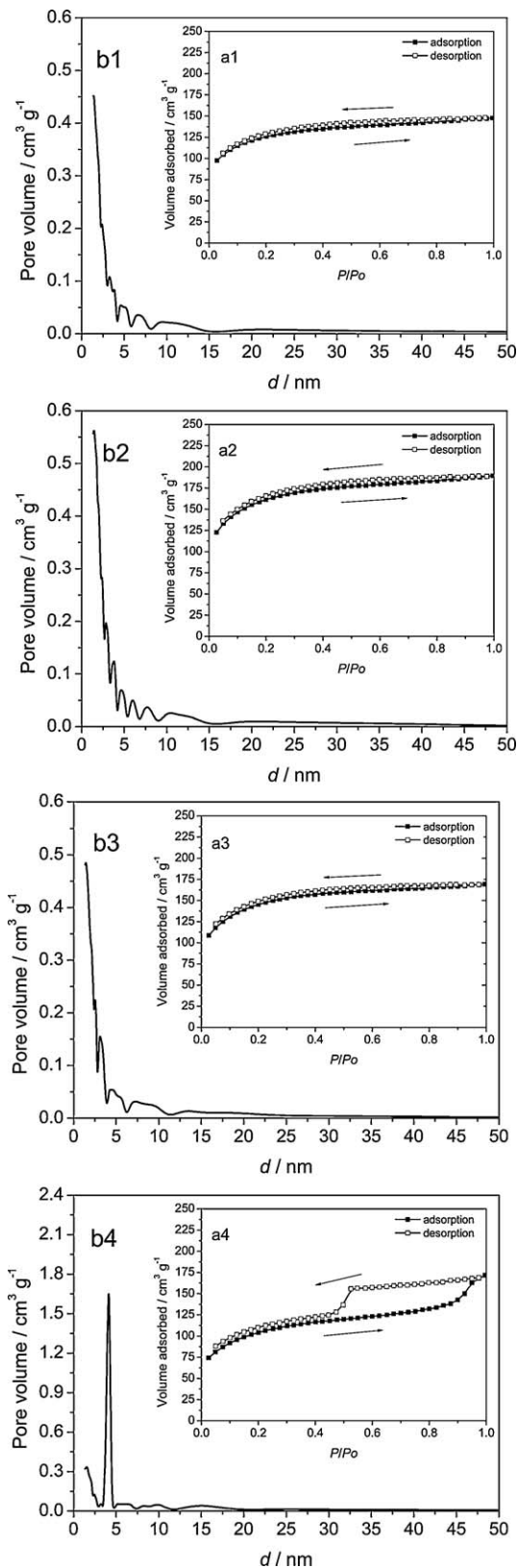


Fig. 5. N_2 -adsorption isotherms (insets: a1–a4) and pore-size distributions (b1–b4) of ceramics pyrolyzed at (1) 1600 °C for 30 min (sample 3), (2) 1650 °C for 30 min (sample 4) (3) 1700 °C for 1 h (sample 5) (4) 1700 °C for 2 h (sample 6) (P/P_0 , relative pressure; d , pore diameter).

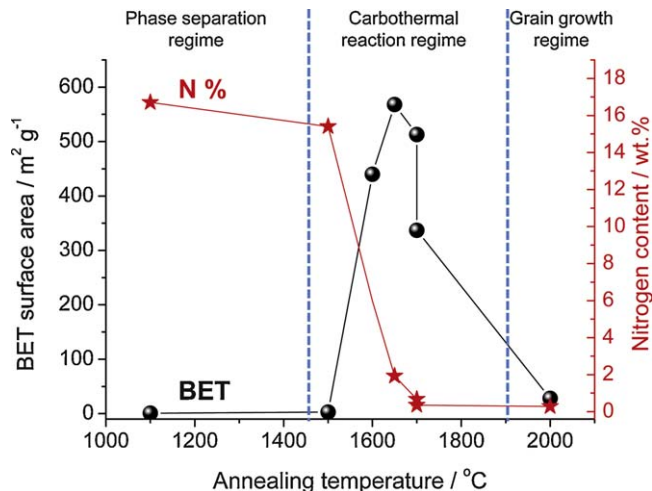


Fig. 6. Correlation between BET specific surface area and the nitrogen content and the corresponding annealing temperatures of 1100 °C (sample 1), 1500 °C (sample 2), 1600 °C (sample 3), 1650 °C (sample 4), 1700 °C (sample 5 and 6) and 2000 °C (sample 7) (as described in Table 1).

The carbon-rich SiCN ceramics reported here are nanostructured materials synthesized by the pyrolysis of phenyl-containing polysilylcarbodiimides.^{15–18} This novel class of ceramics shows multifunctional properties due to the excess of free carbon and have also recently found interesting features in the field of anode materials for Li-ion batteries.^{19,20}

In this publication we report on a simple template-free methodology for tuning porosity of SiCN-ceramics derived from polysilylcarbodiimides utilizing the carbothermal reaction.

2. Materials and methods

Synthesis and pyrolysis of poly(diphenylsilylcarbodiimide). The synthesis of the poly(diphenylsilylcarbodiimide) and the derived ceramics was carried out in purified argon atmosphere as described in Ref. [15]. The samples 3–5 were prepared using two pyrolysis steps as follows: first, the 1 g of prepyrolyzed sample at 1100 °C was heated to 1500 °C (2 h dwelling time) and then post-annealed at the final temperature using different dwelling times: 30 min for samples 3 and 4 and 1 h for sample 5. All the high-temperatures annealing experiments (1500–2000 °C) were performed in an Astro furnace in argon atmosphere (20 psi) in carbon crucibles.

Characterization techniques. High temperature thermogravimetry (HT TG) was performed in He 5.0, 75 ml min^{-1} , using a simultaneous thermoanalyzer Netzsch STA 429 with a heating rate of $2^\circ \text{C min}^{-1}$ (Netzsch Gerätebau GmbH, Selb/Bayern, Germany). Nitrogen adsorption isotherms were measured at 77 K (Model Autosorb-3B, Quantachrome Instruments, USA). Specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Pore size distributions were derived from the desorption branch of the isotherms using Barrett–Joyner–Halenda (BJH) method. Elemental analysis was performed via hot gas extraction using a nitrogen-analyzer (TC-436, Leco Instrumente GmbH, Mönchengladbach, Germany) and via combustion

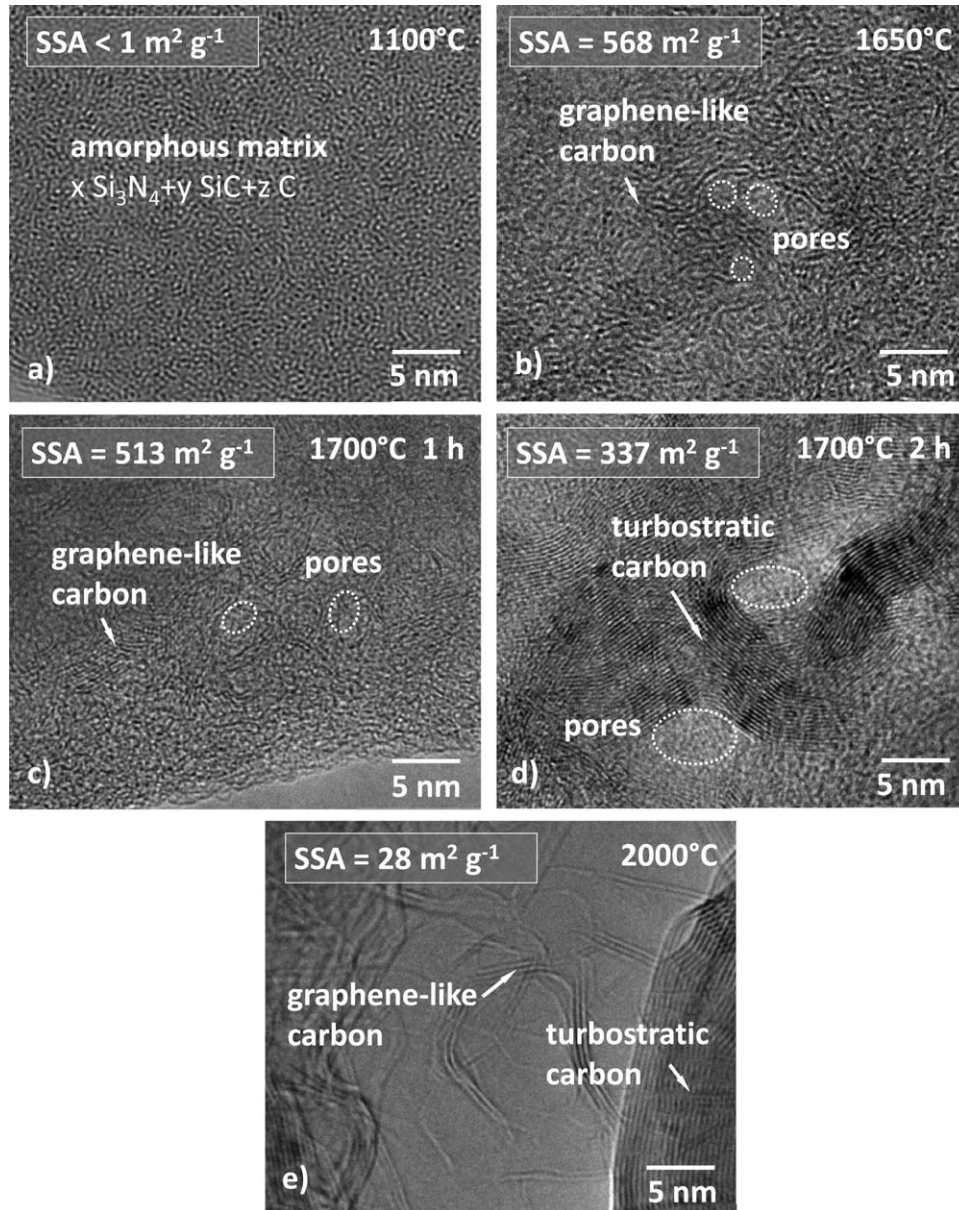


Fig. 7. HRTEM images revealing the microstructure of the carbon phase for the samples annealed at (a) 1100 °C (sample 1); (b) 1650 °C (sample 4); (c) 1700 °C (1 h) (sample 5); (d) 1700 °C (2 h) (sample 6); (e) 2000 °C (sample 7) (as presented in Table 1).

analysis with a carbon-analyzer (C-200, Leco Instrumente GmbH, Mönchengladbach, Germany). Transmission electron microscopy (TEM) was performed using an FEI CM20STEM instrument (FEI, Eindhoven, the Netherlands) operating at an acceleration voltage of 200 kV (wavelength $\lambda = 2.51$ nm). For the TEM sample preparation, the ceramic powders were dispersed in an ultrasonic bath (high purity methanol 99.8%, Sigma–Aldrich Co.) and a small droplet of the suspension was placed on holey carbon (Cu) grit. Upon drying, the samples were lightly coated with carbon to avoid charging under the electron beam.

The X-ray diffraction (XRD) measurements were performed using a Stadi P diffractometer in transmission mode (STOE, Darmstadt, Germany) with Mo $K\alpha$ radiation. Raman spectra were recorded on a confocal Horiba HR800

micro-Raman spectrometer by using an excitation laser wavelength of 514.5 nm.

3. Results and discussion

The ceramic samples were synthesized by the thermal decomposition of poly(diphenylsilylcarbodiimide) at temperatures between 1100 °C and 2000 °C using different annealing times and additional annealing steps as described in the experimental part and in Table 1.

Up to 1450 °C, the carbon-rich SiCN ceramics are composed of three amorphous phases, namely Si_3N_4 , SiC and free C, as displayed schematically in Fig. 1. Above 1450 °C, amorphous Si_3N_4 (*a*- Si_3N_4) reacts with carbon to form amorphous SiC (*a*-SiC) (Eqs. (1a) and (1b)) which transforms afterwards into

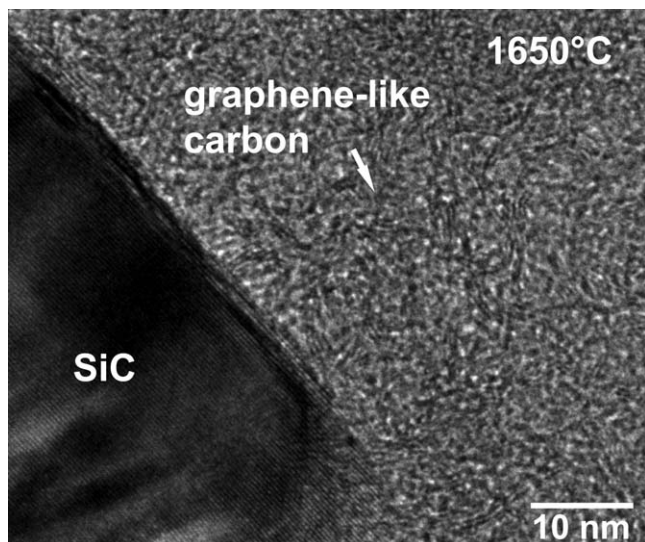
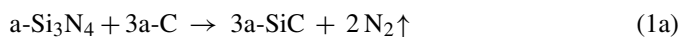


Fig. 8. HRTEM image of the sample 4 annealed at 1650 °C showing the presence of the SiC crystallites embedded in a graphene-like carbon matrix.

α/β -SiC as confirmed by XRD (Fig. 2a). As reported earlier,¹⁵ no crystallization of Si_3N_4 was found to occur under these conditions.



Micro-Raman spectroscopy was used to determine the evolution of free carbon during the thermal decomposition (Fig. 2b). As reported earlier, up to 1500 °C, broad and overlapped D and G bands, characteristic for the amorphous carbon phase, are present. Increasing the temperature to 1700 °C, the D and G bands become sharper and clearly defined. The G' band is observed in the range of 2500–2800 cm^{-1} in defect-free samples and it is very sensitive to the stacking order of the graphene sheets along the c axis. In this study, the G' band increases in intensity with increasing temperature due to a raise in the organization of the free carbon phase. At 2000 °C, the presence of a high amount of turbostratic carbon is underlined by the ratio of the integral intensity of D and G, $I(\text{D})/I(\text{G}) < 1$ and by the shape and intensity of G' relative to the one of the G band. The presence of turbostratic carbon phase is also underlined by the XRD pattern.

The thermal stability of the prepyrolyzed ceramic at 1100 °C was investigated by means of high-temperature thermogravimetry. A relative weight loss of about 19.3% in the range between 1450 and 1900 °C is due to the loss of nitrogen as a result of the carbothermal reaction (see high-temperature TG in Fig. 3). The compositions of the samples studied here (as described in Table 1) are presented also in the ternary composition diagram (Fig. 4). The investigated ceramics are carbon-rich SiCN materials and the nitrogen content of the samples decreases with the temperature of thermolysis and with the increase of the annealing time.

The evolution of nitrogen gas implies the formation of pores and influences the specific surface area. Materials pyrolyzed at

1100 and 1500 °C, **1** and **2**, i.e. at temperatures below those required for the carbothermal reaction, are nonporous (Table 1). Moreover, annealing time is another important factor for the porosity development. In the case of the present system, the pore sizes were found to increase with the annealing time, which is accompanied with a decrease of the specific surface area. Annealing for 2 h at 1700 °C results in porous materials with a high surface area, containing mesopores and micropores, as confirmed by pore-size analysis (Fig. 5b4) and a hysteresis loop in N_2 -adsorption isotherms (sample **6**). Annealing at 2000 °C (same annealing time) leads to a material with a rather low SSA ($28 \text{ m}^2 \text{ g}^{-1}$) (sample **7**). At temperatures above 1900 °C, as the carbothermal reaction is finished and all nitrogen has been out-gassed, grain growth and densification processes, which imply a decrease in the surface free energy, lead to a decrease in the SSA.

To investigate the conditions of micropore and mesopore formation, several specimens have been annealed over different times at the temperatures corresponding to the regime of the carbothermal reaction (see Table 1). A relatively short annealing time of the samples pre-annealed (**2**, at 1500 °C) and heat-treated at intermediate temperatures (**3** and **4**, at 1600 and 1650 °C, respectively) leads not only to a significant increase in the SSA of the samples, up to 440 and $568 \text{ m}^2 \text{ g}^{-1}$, respectively, but also changes the pore size distribution. N_2 -adsorption isotherm of both specimens are type-I isotherms which are related to the microporous nature of the materials (Fig. 5). The carbon-rich SiCN ceramics exposed to the carbothermal reaction at 1650 °C develop a SSA as high as $568 \text{ m}^2 \text{ g}^{-1}$ with a micropore volume of $0.22 \text{ cm}^3 \text{ g}^{-1}$.

From 1650 to 2000 °C, the pores increase in average size but decrease in volume fraction as the pyrolysis temperature is increased. As reported in the case of other polymer-derived ceramics,^{21,22} this thermodynamically favorable decrease in specific surface area appears to occur due to a viscous flow process of the residual amorphous phase.

The strong correlation between the nitrogen content and the SSA of the samples (Fig. 6) points out that the key factor in the formation of the porous structure is the evolution of nitrogen gas as a result/product of the carbothermal reaction. This correlation is valid only for temperatures corresponding to the regime of this reaction; no correlation was found for samples annealed either below, where the carbothermal reaction does not occur, or above this temperature where all nitrogen is consumed.

Compared to the reported low-temperature synthesized macroporous polysilazane-derived ceramics,^{23,24} it is obvious that the decomposition of polysilylcarbodiimides-derived ceramics, composed of nanodomains of 1–3 nm in size and containing no mixed bonds, is yielding a microporosity and/or mesoporosity when the materials are heated to temperatures where the carbothermal reaction is taking place. It seems that the domains size is a key factor for the formation of small pores (micro- and mesopores) in the case of nanodomains and of the macropores in the case of large domains.

One important characterization tool for the local structural rearrangements in polymer-derived ceramics is transmission electron microscopy (TEM).^{25–27} The micro/nanostructure of

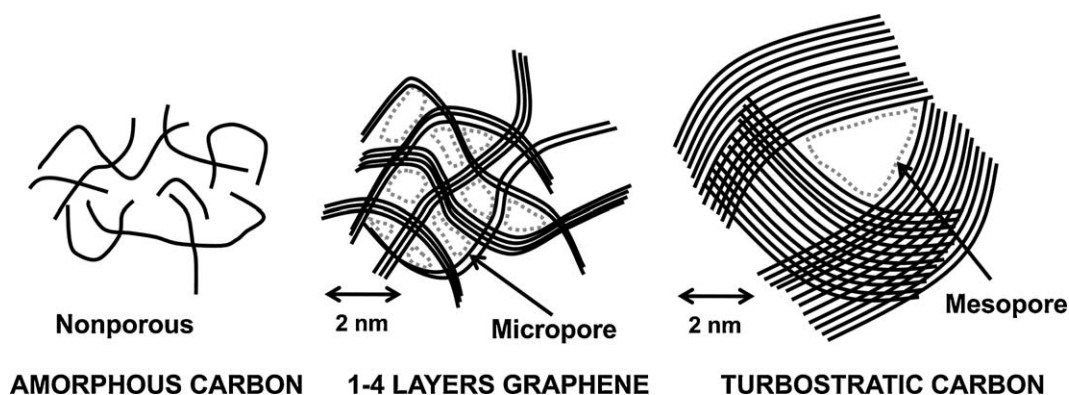


Fig. 9. Schematic representation of the dependence of pore size on the graphene organization.

the samples prepared at 1100 (1), 1650 (4), 1700 (5 and 6) and 2000 °C (7) were characterized by high-resolution TEM (HRTEM), as shown in Fig. 7a–e. The sample 1 at 1100 °C shows no indication of any crystalline phase (Fig. 7a). Special attention was given to the sample 4 with the highest SSA obtained via annealing at 1650 °C for 0.5 h ($568 \text{ m}^2 \text{ g}^{-1}$) (Fig. 7b). This ceramic is composed of α/β -SiC crystallites, homogeneously dispersed throughout the matrix as shown in Fig. 8. The latter solely consists of graphene-like carbon, which, as a consequence, yields the high specific surface area monitored for this material, since graphene-like carbon is structurally disorganized and allows a high pore volume between the wound graphene stacks.

Very interesting is also the comparison between the samples 5 and 6 prepared at the same temperature (1700 °C), but with different annealing times of 1 h and 2 h, respectively. Sample 5 reveals the same particular microstructure as sample 4, where SiC crystallites are embedded in a matrix of graphene-like carbon (Fig. 7c). In the carbon phase, small micropores (diameter $\sim 2 \text{ nm}$) can be distinguished. Preparing the sample with 2 h dwelling time (sample 6), the carbon phase remains amorphous only in close proximity of SiC. In the rest of the material, the carbon phase is turbostratic incorporating mesopores between the stacks (Fig. 7d). The increase in the size of the pores from micro- to mesopores seems to be correlated to the increase in the number of graphene layers. A low number of graphene layers can accommodate small micropores between the stacks (samples 4 and 5) and large number of graphene layers like in turbostratic phase (more than 10 layers graphene) lodge large mesopores between the stacks (sample 6). The diameter of the pores and the number of graphene layers increase with increasing the dwelling time.

At 2000 °C, only large SiC crystallites surrounded by two types of carbon phase, namely graphene-like and turbostratic, can be observed. Due to the integral nature of micro-Raman spectroscopy, the presence of graphene-like carbon was not possible to be identified by this method. It is assumed that the bands corresponding to graphene phase perfectly overlapped with the ones of turbostratic carbon. Another problem is the nature of the second-order G' band. In the case of turbostratic carbon, there is no stacking order between adjacent layers and therefore there is a very weak interaction between the graphene planes so that

turbostratic carbon can be considered to be a 2D graphite, similar to a graphene layer.

At 2000 °C the carbothermal reaction is finished and the micro- and mesopores are not observed anymore. Fig. 7e presents the differences between the graphene-like carbon in sample 7 with 1–4 layers graphene and the turbostratic carbon phase with 10–20 layers of graphene.

As shown by HRTEM analysis, the micro- and mesopores are located only in the carbon phase and their diameter seems to depend on the organization of graphene layers of the free carbon as shown schematically in Fig. 9. No correlation between the pore sizes and the α/β -SiC crystallite sizes was observed in our samples, as shown in Table 1.

4. Conclusions

Ceramics with a high specific surface area and defined pore sizes can be easily synthesized by means of thermal decomposition of SiCN ceramics obtained from carbon-rich polysilylcarbodiimides. The variation of the thermolysis parameters, namely temperature, annealing time and additional annealing steps is the key factor to manipulate the porosity features. Using the thermal decomposition process, the ceramics develop a SSA as high as $568 \text{ m}^2 \text{ g}^{-1}$ with the volume of micropores of $0.22 \text{ cm}^3 \text{ g}^{-1}$, when pyrolyzed at 1650 °C. HRTEM confirmed that the micro/nanostructure is composed of SiC homogeneously dispersed in a graphene-like carbon matrix and the pores are associated with the carbon phase. The pore diameters appear to be dependent on the organization of graphene layers and not on the crystallite sizes of β -SiC.

The reported ceramics are chemically inert and made from pure precursors without using any additives. The novel porous materials can find applications as catalyst support at high temperatures, selective gas separation and purification membranes, for hydrogen storage and other analogous applications.

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