



In situ synthesis of Si₂N₂O/Si₃N₄ composite ceramics using polysilyloxycarbodiimide precursors

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Abstract

In situ synthesis of Si₂N₂O/Si₃N₄ composite ceramics was conducted via thermolysis of novel polysilyloxycarbodiimide ([SiOSi(NCN)₃]_n) precursors between 1000 and 1500 °C in nitrogen atmosphere. The relative structures of Si₂N₂O/Si₃N₄ composite ceramics were explained by the structural evolution observed by electron energy-loss spectroscopy but also by Fourier transform infrared and ²⁹Si-NMR spectrometry. An amorphous single-phase Si₂N₂O ceramic with porous structure with pore size of 10–20 μm in diameter was obtained via a pyrolyzed process at 1000 °C. After heat-treatment at 1400 °C, a composite ceramic was obtained composed of 53.2 wt.% Si₂N₂O and 46.8 wt.% Si₃N₄ phases. The amount of Si₂N₂O phase in the composite ceramic decreased further after heat-treatment at 1500 °C and a crystalline product containing 12.8 wt.% Si₂N₂O and 87.2 wt.% Si₃N₄ phases was obtained. In addition, it is interesting that residual carbon in the ceramic composite nearly disappeared and no SiC phase was observed in the final Si₂N₂O/Si₃N₄ composite.

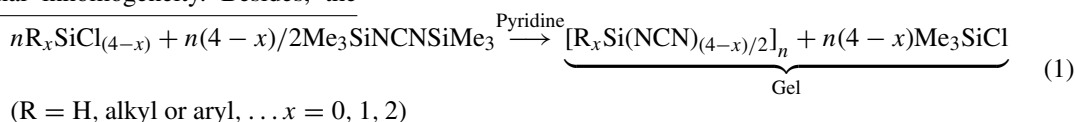
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1. Introduction

Silicon nitride (Si₃N₄) and silicon oxynitride (Si₂N₂O) due to their excellent physicochemical and thermomechanical properties, are two of the most attractive materials for the preparation of porous ceramic materials for a broad range of engineering applications, demanding high strength, low density, high surface area, high permeability, low specific heat and high thermal insulation. Si₂N₂O can optimize the properties of Si₃N₄ materials and develop a series of excellent composite ceramics. Usually, Si₂N₂O/Si₃N₄ composite ceramics using the mixture of Si₃N₄ and SiO₂ powders at the high sintering temperature around 1700 °C,^{1,2} is prepared by conventional solid state reaction which often results in high agglomeration, particle coarsening, and compositional inhomogeneity. Besides, the

multi-pass extrusion process has been used for the fabrication of porous Si₃N₄/Si₂N₂O bodies, using a nitridation process at 1400 °C in flowing N₂ gas for 20 h.^{3,4} Furthermore, an investigation on the microstructure and mechanical properties of Si/Si₃N₄/Si₂N₂O porous ceramic composites, synthesized in a multi-step approach via hybrid precursor system chemical vapor infiltration and direct nitridation has been conducted.⁵ Alternative chemical direct synthesis route has been proposed including the precursor-derived ceramics process. For example, the non-oxide precursor derived ceramics can be fabricated by poly(silylcarbodiimide) (PSCN, [R_xSi(NCN)_{(4-x)/2}]_n) sol-gel method. Non-oxide SiCN ceramics have been fabricated via this novel sol-gel method with the reaction of 2–4-chlorosilane and bis(trimethylsilyl)carbodiimide (see equation 1)^{6–14}



(R = H, alkyl or aryl, ... x = 0, 1, 2)

In comparison with conventional solid state method, chemical methods have several advantages, such as low processing temperature, better control of composition, homogeneity, purity,

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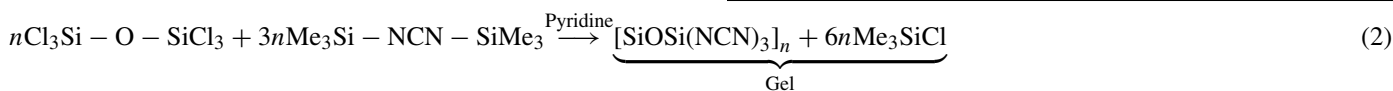
and potentially reproducible properties. The most attractive feature of the precursor-derived ceramics is the low processing temperature as low as 800–1000 °C, high purity and good high-temperature properties.^{15–18} Thus, it is still a challenge to investigate the fabrication of Si₂N₂O/Si₃N₄ composite ceramics via the in situ precursor-derived ceramics process.

Herein, polysilyloxycarbodiimide precursors [SiOSi(NCN)₃]_n were synthesized firstly via the controlled insert of oxygen into [R_xSi(NCN)_{(4-x)/2}]_n structure according to this carbodiimide sol–gel process. In situ synthesis of Si₂N₂O/Si₃N₄ composite ceramics was conducted via the thermolysis of the novel polysilyloxycarbodiimide precursors between 1000 and 1500 °C in nitrogen atmosphere. An amorphous single-phase Si₂N₂O ceramic with porous structure was obtained via a pyrolyzed process at 1000 °C. After heat-treatment at 1400 °C, a composite ceramic was obtained composed of 53.2 wt.% Si₂N₂O and 46.8 wt.% Si₃N₄ phases. The amount of Si₂N₂O phase in the composite ceramic decreased further after heat-treatment at 1500 °C and a crystalline product containing 12.8 wt.% Si₂N₂O and 87.2 wt.% Si₃N₄ phases was obtained. In addition, in comparison with the polymer derived SiCN ceramics fabricated by the analogous carbodiimide sol–gel process,^{6–14} it is interesting that residual carbon in the ceramic composite nearly disappeared and no SiC phase was observed in the final Si₂N₂O/Si₃N₄ composite at high temperature.

2. Experimental

All reactions were carried out in a glove box or in purified flowing argon using standard Schlenk techniques.¹⁹ Hexachlorodisiloxane (Cl₃Si–O–SiCl₃, Sigma–Aldrich Chemie GmbH, 96%) and bis(trimethylsilyl)carbodiimide (BTSC, (CH₃)₃SiN=C=NSi(CH₃)₃) were used as starting materials for the synthesis of poly(silyloxycarbodiimide) (PSOCN, [SiOSi(NCN)₃]_n). BTSC was synthesized according to the literature²⁰: a mixture of hexamethyldisilazane (Me₃Si–NH–SiMe₃, Sigma–Aldrich Chemie GmbH, 99%) (177 g), cyanamide ((H₂N–CN)₂, Sigma–Aldrich Chemie GmbH, 99%) (42 g), and ammonium sulfate ((NH₄)₂SO₄, Sigma–Aldrich Chemie GmbH, 99%) (0.2 g) was heated to reflux for 8 h. Distillation twice over a Vigreux column at 164 °C gave 134 g (72%) BTSC. Toluene and pyridine were purified and stored in the glove box, using as the solvent and catalyst for the synthesis of PSOCN.

1:3 molar ratio of Cl₃Si–O–SiCl₃ and (CH₃)₃SiN=C=NSi(CH₃)₃ was used to synthesize PSOCN (see Eq. (2)). The basic structure unit of PSOCN is [SiOSi(NCN)₃]_n with by-product of (CH₃)₃SiCl.



Hexachlorodisiloxane (5.0 mL, 27.2 mmol) was dropped slowly into excess BTSC (23.9 mL, 108.8 mmol) under strong magnetic stirring. 3.5 vol.% pyridine (molar ratio of Py/BTSC = 0.20) was added to the mixture and resolved in 20 mL toluene. The

solution of mixture appears yellow. Small amount of white sedimentation was observed at the bottom of Schlenk flask, ascribed to the adduct of hexachlorodisiloxane and pyridine (Cl₃Si–O–SiCl₃·2Py).^{21,22} The solution of the mixture was stirred for 1 h, and then first heated to reflux at 120 °C for 12 h, and second to 160 °C for 12 h. When the color of solution became to dark red, the extraction in a vacuum was performed. The by-product (CH₃)₃SiCl, toluene and excess BTSC were removed. Then the obtained solid was heated to cross-link further at 160 °C/10⁻² mbar Ar for 2 h to get the final yellow xerogel-like solid product.

For the pyrolysis of the samples, the polymeric precursor was filled in a quartz crucible. The crucible was put in the middle part of a quartz tube. The quartz tube was sealed and heated under a steady flow of ultra-high-purity nitrogen (99.9999%, 5 L/h) in a programmable horizontal tube furnace with a heating ramp of 5 °C/min to 1000 °C for 5 h and free-cooling to the room temperature. Gray SiCON ceramics were obtained, with 20 vol.% shrinkage compared to PSOCN xerogel. For the thermolysis up to 1500 °C, the pyrolyzed samples were heated in the middle part of an alumina furnace under nitrogen atmosphere (99.9999%, 5 L/h) first at 10 °C/min to 1000 °C, and then at 5 °C/min to 1400 or 1500 °C for 5 h, respectively, followed by free-cooling to the room temperature. Black ceramics were obtained with 3 vol.% shrinkage compared to SiCON ceramics pyrolyzed at 1000 °C.

Thermogravimetric analysis (TG) of the SiCON precursor was performed at 5 °C/min under nitrogen (99.9999%) flow on TG/DTA 22, while the releasing gas species during this process were detected via in situ mass spectrometer. The chemical structure of samples was analyzed by fourier transform infrared spectrometer (FT-IR) spectra using the KBr pellets method on Varian Excalibur 3100 with resolution of 4 cm⁻¹ and solid-state NMR technique on Bruker Avance TM WB 400 MHz spectrometer with a resonance frequency of 79.51 MHz. SEM (LEO 1530 FEG, Karl Zeiss NTS GmbH, Germany) with energy dispersive spectroscopy (EDS) was used to characterize the microstructure and relative weight percentage of chemical element of the materials and local microstructure evolution at higher temperatures was observed by HR-TEM using a CM 20 FEG electron microscope with operating voltage of 200 kV (Philips, Eindhoven, Netherlands), coupled with a post-column electron energy filter of Gatan Imaging Filter GIF 200 and model 667 (Pleasanton, CA). The pore size distribution of the as-prepared samples were employed by Fully automated Mercury Porosimeters (PASCAL 440, POROTEC GmbH). Chemical elemental composition of the ceramics was analyzed by elemental analyzer. In addition, the inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted for element measurement. The crystalline

behavior of the ceramics were investigated by X-ray diffraction (Siemens D5000 using Cu-K_α radiation, step size per time: 0.02 theta/s).

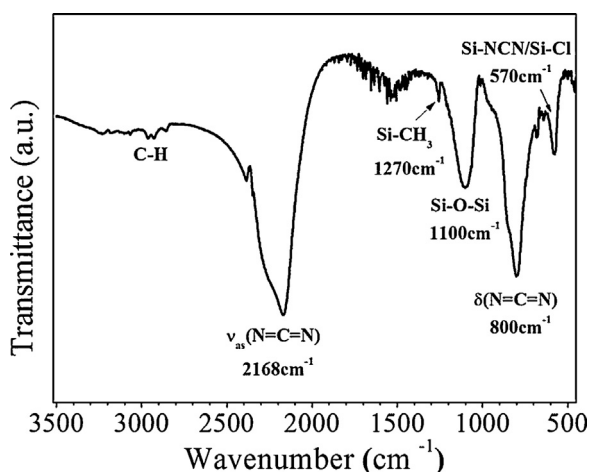


Fig. 1. FTIR spectra of the as-prepared PSOCN xerogel.

3. Results and discussion

3.1. Synthesis of poly(silyloxycarbodiimide) precursor

Poly(silyloxycarbodiimide) (PSOCN) is a polymer gel-like solid with basic structure unit $[\text{SiOSi}(\text{NCN})_3]_n$. Fig. 1 shows the FT-IR spectra of PSOCN xerogel. The main absorption band at 1100 cm^{-1} can be assigned to Si–O stretching vibration, 2168 cm^{-1} for $[\text{N}=\text{C}=\text{N}]$ asymmetric stretching vibration, and 800 cm^{-1} for $[\text{N}=\text{C}=\text{N}]$ bending vibration, confirming that Si–O–Si is coordinated to $\text{N}=\text{C}=\text{N}$ units in the products, which is in agreement with the previous works.^{10–12}

The weak absorption band at 1270 cm^{-1} is due to Si–CH₃ deformation vibration, 570 cm^{-1} for Si–NCN or Si–Cl stretching vibration, $\sim 2900\text{ cm}^{-1}$ for C–H stretching vibration. They may arise from residual by-product $(\text{CH}_3)_3\text{SiCl}$ and excess BTSC ($(\text{CH}_3)_3\text{SiN}=\text{C}=\text{NSi}(\text{CH}_3)_3$) in the process of synthesis of PSOCN gel (see Eq. (2)).¹¹ Based on the above-mentioned results, the chemical structure of SiCON xerogel was proposed,

as shown in Fig. 2. This structure of SiCON xerogel could be beneficial to understand the relationship between the chemical structure and pore distribution of SiCON ceramics after post-pyrolysis heat treatment.

3.2. Thermolysis of poly(silyloxycarbodiimide) precursor

Fig. 3a shows the SEM image of the SiCON ceramic pyrolyzed at $1000\text{ }^\circ\text{C}$ in nitrogen atmosphere. It also can be seen that porous ceramic matrix is dispersed by about $10\text{ }\mu\text{m}$ in diameter of pores with porosity of 60%. In order to further investigate the micro structure of the SiCON ceramic in detail, the TEM image of the relative SiCON ceramic is presented in Fig. 3b, indicating that a large number of homogeneous nanopores with an average range of diameter between 10 and 20 nm are distributed in the SiCON ceramic matrix. In addition, the pore size distribution has also been analyzed by the Mercury intrusion porosimetry, as shown in Fig. 4, which is in agreement with the results from the SEM analysis. Thus, the as-prepared SiCON ceramic at $1000\text{ }^\circ\text{C}$ is a multigrade nano-micron porous structure. However, polymeric Si/C/O/N xerogels were prepared via the static route in an oven at $45\text{--}90\text{ }^\circ\text{C}$ for 7–30 days and then the precursor for the nanoporous ceramic appears a totally dense gel structure.²¹ In comparison, the precursor produced in this work by refluxing at higher temperature possesses a loosen structure, which could be applied for gas separation, water purification, catalytic carriers, etc.

In order to understand the pyrolysis process of the SiCON precursor polymer, the thermogravimetric analysis (TG) and in situ mass spectrometry (MS) from room temperature to $1500\text{ }^\circ\text{C}$ in nitrogen atmosphere were employed, as shown in Figs. 5 and 6, respectively. It can be observed that the derived SiCON ceramic yield is 64% from Fig. 4. Below $400\text{ }^\circ\text{C}$, a mass loss of the derived SiCON ceramic is about 10%, deducting that the as-prepared sample could be released by-product trimethylchlorosilane and its decomposition fragments in comparison with the previous reaction of other chlorosilanes and

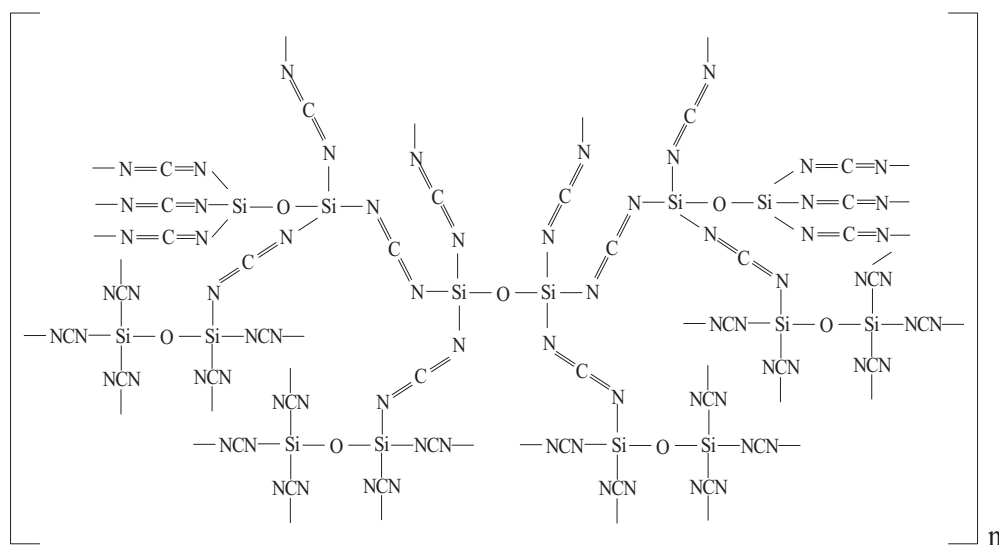


Fig. 2. Proposed molecular structure of the polysilyloxycarbodiimide xerogel.

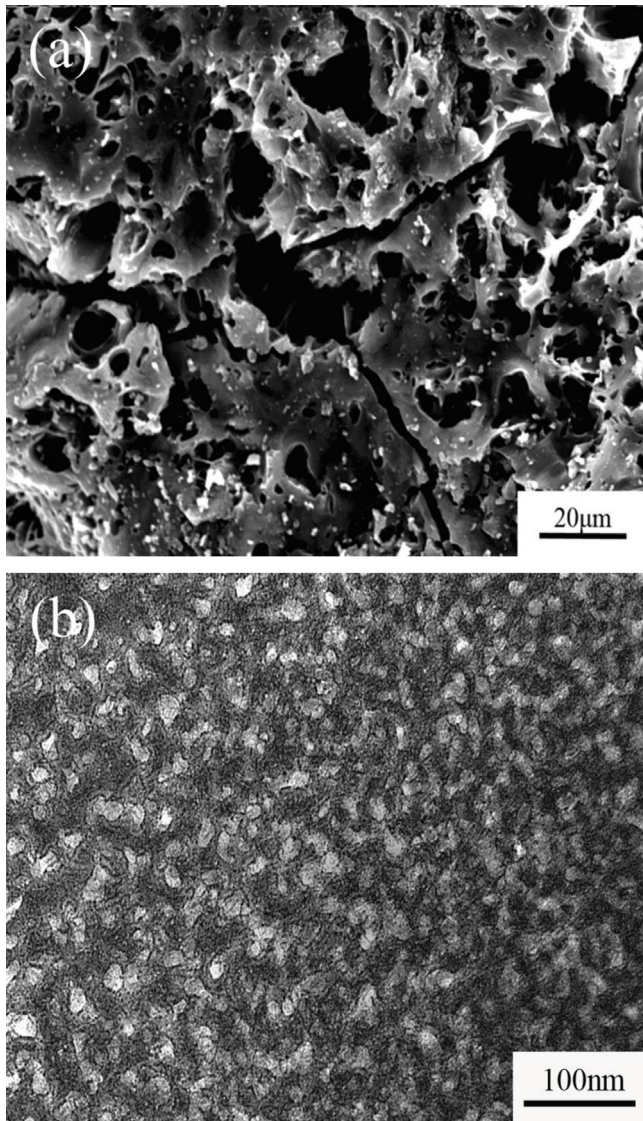


Fig. 3. SEM and TEM images of the as-prepared SiCON ceramics at 1000 °C.

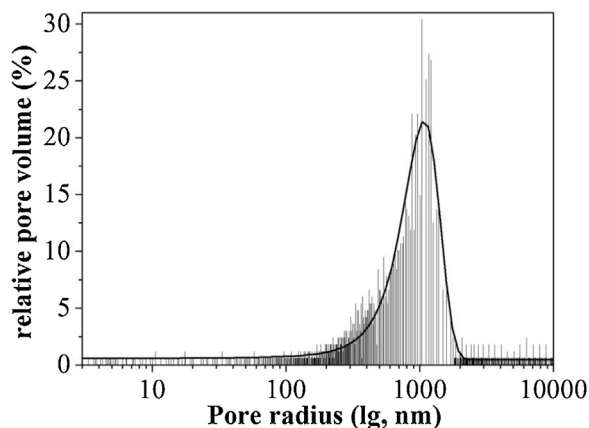


Fig. 4. Pore size distribution derived by Mercury intrusion porosimetry for the as-prepared SiCON ceramics at 1000 °C.

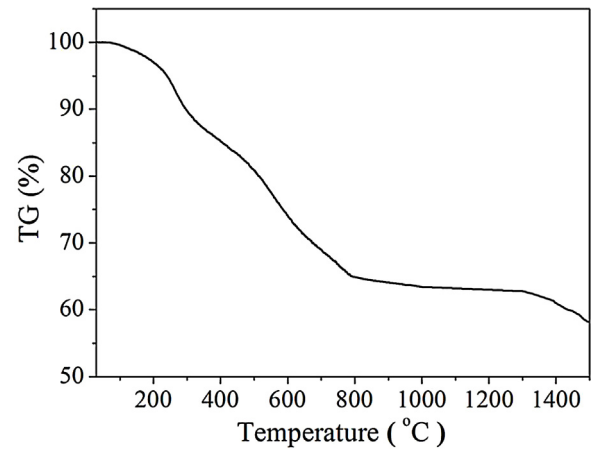


Fig. 5. Thermogravimetric analysis of as-prepared PSOCN xerogel in nitrogen atmosphere.

BTSC.¹⁴ Between approximately 400 and 800 °C, it can be seen from Fig. 6 that a second thermal reaction occurs via a series of characterization using elimination of methane (CH_x $m/z = 16, 15, 14, 13$), nitriles (HCN $m/z = 27$, $\text{CH}_3\text{-CN}$ $m/z = 41$), carbon monoxide (CO $m/z = 28$) and hydrogen (H_2 $m/z = 2$), producing a weight loss about 26%. The methane, hydrogen cyanide, acetonitrile and hydrogen could be ascribed to the decomposition fragments of the end groups $-\text{[NCNSi(CH}_3\text{)]}_3$ from large xerogel molecular structure $[\text{SiOSi(NCN)}_3]_n\text{-[NCNSi(CH}_3\text{)]}_3$. However, CO can be detected in this system, while it can not be detected in the case of $[\text{RSi(NCN)}_{1.5}]_n$ ($\text{R}=\text{H, alkyl-, aryl-...}$).^{7,9} The difference might exist in the backbone structure unit of poly(silyloxycarbodiimide) $[\text{SiOSi(NCN)}_3]_n$ and poly(silylcarbodiimide) $[\text{RSi(NCN)}_{1.5}]_n$. At 1000–1500 °C, the weight loss is about 7%, which is due to the releasing of nitrogen and carbon monoxide at high temperature. This part will be discussed in the later part of the text.

3.3. Microstructure and chemical structure of SiCON ceramics at high temperature

The crystallization behavior of the SiCON ceramics derived from precursor polysilyloxycarbodiimide was investigated by X-ray diffraction (XRD), as shown in Fig. 6. It can be seen

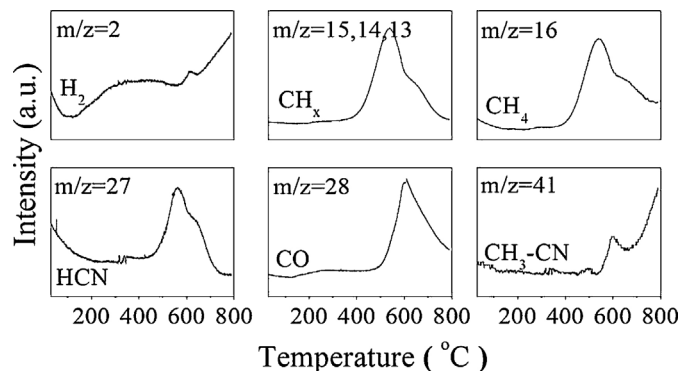


Fig. 6. The gas species released during thermolysis process of the as-prepared PSOCN xerogel by Mass spectrometry.

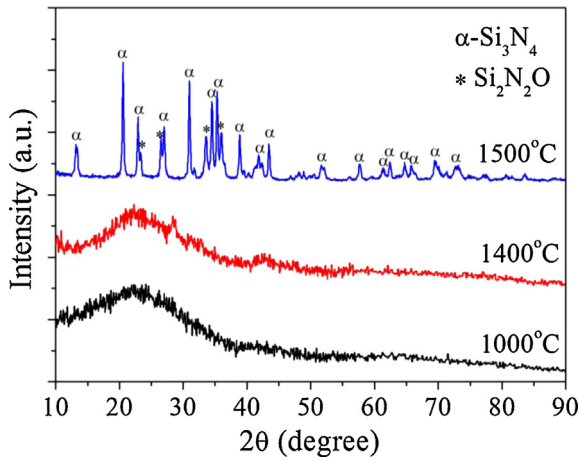


Fig. 7. XRD patterns of the as-prepared ceramics at 1000, 1400 and 1500 °C.

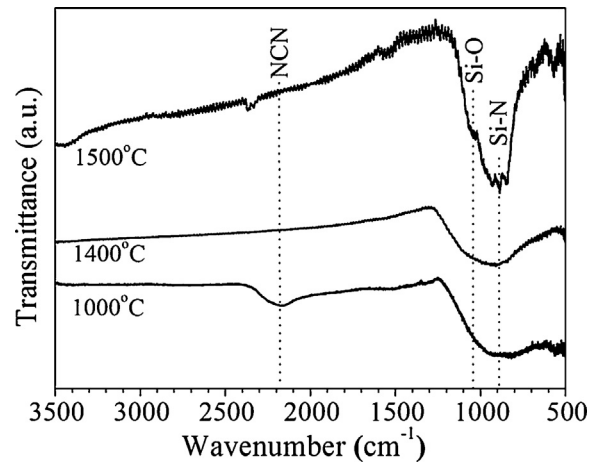


Fig. 8. FTIR spectra of the as-prepared ceramics at 1000, 1400 and 1500 °C.

that an amorphous SiCON ceramic was obtained between 1000 and 1400 °C. After heat treatment at 1500 °C, the distinct sharp peaks in Fig. 7 showed the high crystallinity and the complete formation of the α - Si_3N_4 phase (space group: P31c; JCPDS card no. 41-0360),²³ corresponding the major peaks at $2\theta = 20.55, 30.96, 34.52$ and 35.29° for the diffractions of the (101), (210), (102) and (201) plane. Besides, the intensity for several additional peaks at 2θ of $26.48, 34.21$ and 35.85° for another phase was indexed the phase of $\text{Si}_2\text{N}_2\text{O}$, corresponded to the diffractions of the (111), (020) and (310) plane of an orthorhombic phase of $\text{Si}_2\text{N}_2\text{O}$ phase (JCPDS Card, No 47-1627) with space group Cmc2₁ were observed in the final composites. In order to ascertain the weight percentage of α - Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ crystals in the composites, the phase semi-quantitative analysis by XRD was employed in these ceramic composites. Besides, the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and energy dispersive spectroscopy (EDS) for silicon and oxygen element analysis were conducted in this work. Combined with ICP, EDS and the phase semi-quantitative analysis, it is confirmed that the composite after post-pyrolysis heat treatment at 1500 °C is consisted with 90 wt.% Si_3N_4 and 10 wt.% $\text{Si}_2\text{N}_2\text{O}$ crystals.

In order to further ascertain the chemical components of as-prepared ceramics, elemental analyzer was employed. Table 1 shows the elemental compositions of SiCON ceramics after thermolysis between 1000 and 1500 °C in nitrogen atmosphere. At 1000 °C, the composition of ceramic is $\text{SiN}_{1.80}\text{C}_{1.16}\text{O}_{0.47}$. At 1400 °C, the composition of ceramic is $\text{SiN}_{1.63}\text{C}_{0.49}\text{O}_{0.33}$, close to 53.2 wt.% $\text{Si}_2\text{N}_2\text{O}$ phase and 46.8 wt.% Si_3N_4 phase. At 1500 °C, the composition of ceramic is $\text{SiN}_{1.25}\text{C}_{0.04}\text{O}_{0.06}$, close to 12.8 wt.% $\text{Si}_2\text{N}_2\text{O}$ and 87.2 wt.% Si_3N_4 . It can be seen from the chemical formula between 1000 and 1500 °C, the content of Nitrogen, carbon and oxygen all decrease gradually and the content of carbon and oxygen nearly disappear. $\text{Si}_2\text{N}_2\text{O}$ tends to decompose above 1400 °C (see Eq. (3))^{24–26} and it can also react with free carbon in the SiCON material matrix, which causes decrease of carbon content and the transformation of $\text{Si}_2\text{N}_2\text{O}$ to

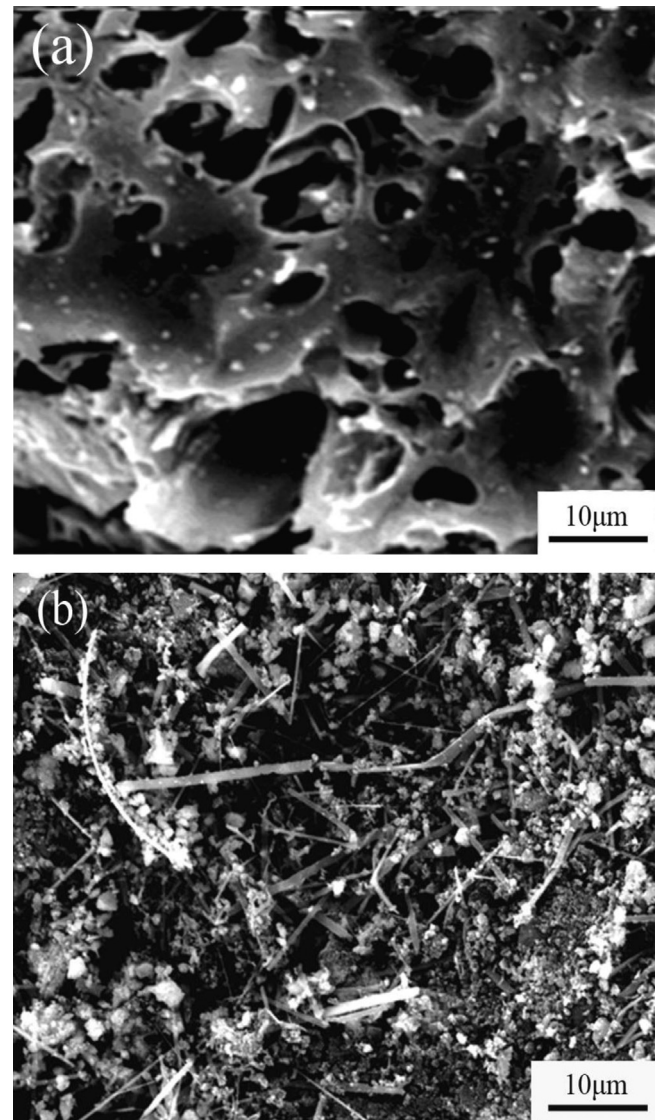
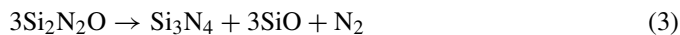


Fig. 9. SEM images of the as-prepared SiCON ceramics at 1400 (a) and 1500 °C (b).

Table 1
Chemical elemental analysis data of the as-prepared ceramics at 1000, 1400 and 1500 °C.

Temperature (°C)	Composition (wt.%)				Empirical formula
	Si	C	N	O	
1000	36.9	18.4	33.7	10.0	SiN _{1.80} C _{1.16} O _{0.47}
1400	45.1	9.5	36.7	8.7	SiN _{1.63} C _{0.49} O _{0.33}
1500	59.7	1.0	37.4	1.9	SiN _{1.25} C _{0.04} O _{0.06}

Si₃N₄ (see Eq. (4)) at 1500 °C. The relative equations have been shown below.



FT-IR spectra of the thermolysis products obtained between 1000 and 1500 °C are shown in Fig. 8. It may be deduced that the pure Si₂N₂O phase was obtained at 1000 °C, corresponding to Si–N–O band at about 1100 cm⁻¹. With the increase of heating temperature from 1400 to 1500 °C, the main composition of ceramics is composed of Si₂N₂O and Si₃N₄ phases,

corresponding to Si–O band at 1100 cm⁻¹ and Si–N band at about 900 cm⁻¹.

The asymmetric stretching bond of the carbodiimide (N=C=N) group at 2192 cm⁻¹ is found in the ceramic at 1000 °C, indicating that a fraction of PSOCN gel structure remains in the ceramic matrix. According to the results by chemical elemental analysis, Si₂N₂O (NCN) is the composition of the ceramic at this temperature. At 1400 °C, [N=C=N] band disappears and only a strong absorption band around 1000 cm⁻¹, which can be assigned to Si–O at 1100 cm⁻¹, Si–N at 980 cm⁻¹ and 860 cm⁻¹. At 1500 °C, the broad peak splits into several small sharp peaks at about 900 cm⁻¹, indicating the main absorption band is Si–N.

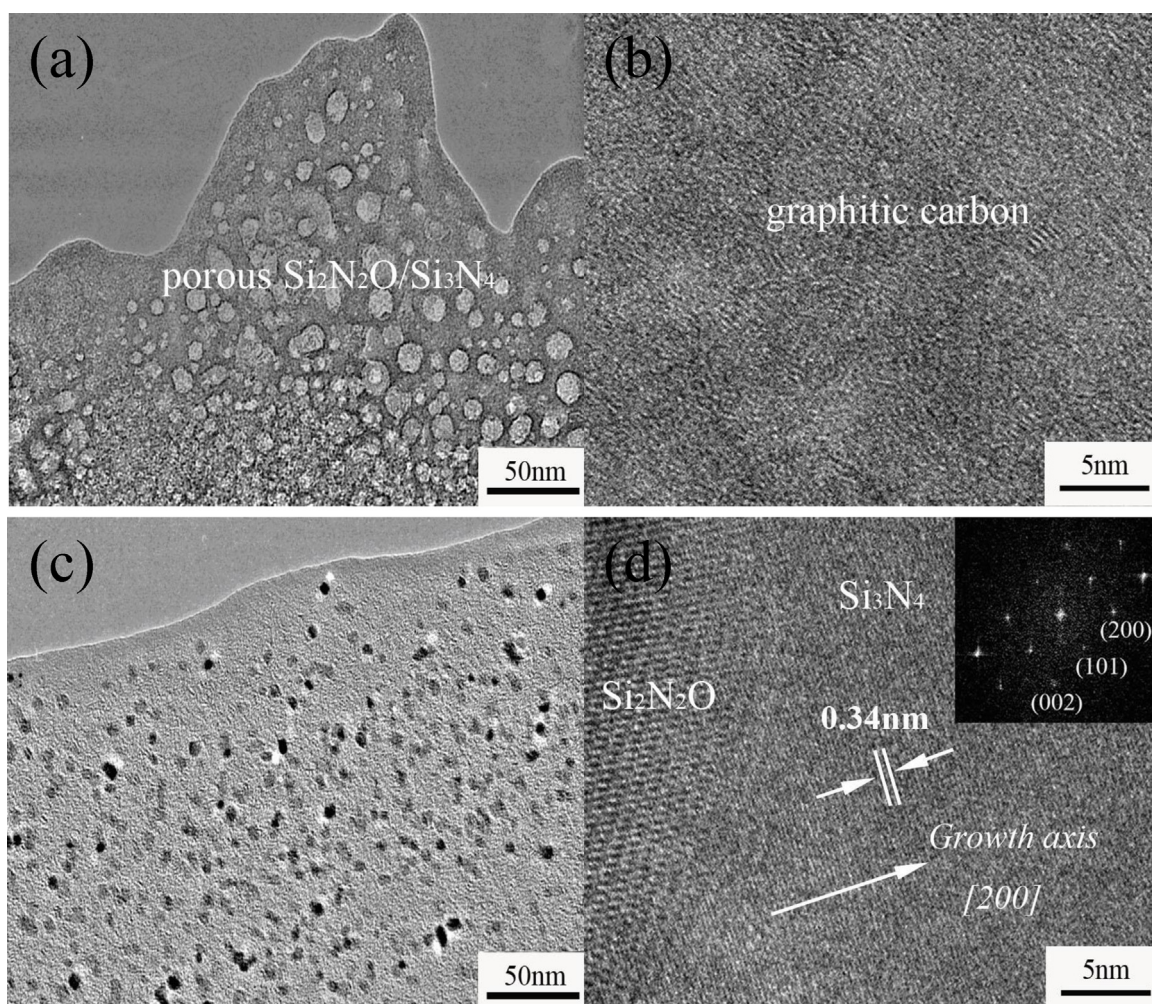


Fig. 10. TEM images of the as-prepared ceramics at 1400 (a) and 1500 °C (b).

The SEM images of ceramics after heat treatment at 1400 and 1500 °C are shown in Fig. 9a and b. At 1400 °C, the ceramic remains a porous structure with pore sizes of 1–10 μm in diameter and 20% porosity. The pore size and porosity are both less than that of the sample pyrolyzed at 1000 °C. At 1500 °C, the ceramic becomes dense further and some Si₃N₄ nanorods of 50–500 nm in diameter were observed in the residue pores. Thus, it can be deduced that the ceramic composites become densification with the increasing of the temperature. The remaining porous structure is beneficial to the formation of Si₃N₄ nanorods.

The microstructure evolution of ceramics after heat treatment at 1400 and 1500 °C was investigated by high-resolution TEM (HRTEM) microscopy, shown in Fig. 10a–d. At 1400 °C, the ceramic keeps an amorphous porous matrix (Fig. 10a) with free carbon phase (Fig. 10b). At 1500 °C, the ceramics revealed a ~70% crystallization matrix with ~5 nm crystals of Si₂N₂O and Si₃N₄ phases and no SiC phase (Fig. 10c and d). According to the results of X-ray diffraction and chemical elemental analysis, the composition of crystals is ~90% Si₃N₄ and ~10% Si₂N₂O. No crystalline SiC phase was found, which is in contrast to the PSCN ceramics.²⁷ It may be ascribed to the different carbon and oxygen content in the precursors of PSOCN and PSCN. In this work, the existence of Si₂N₂O phase consumes free carbon in the SiCON material matrix, causing disappearance of carbon phase. Compared with the previous work,^{6–14} it is interesting that no SiC phase can be found in the resulting products.

In addition to HRTEM images, electron-energy-loss structure (EELS) studies of the Si–L_{2,3}, N–K and O–K ionization edges were performed at the very same regions of HRTEM images recording, in order to characterize the local chemical environment within the material matrix, as shown in Fig. 11. In the EELS spectra of the Si–L_{2,3} Si–L_{2,3},²⁴ at 1000 °C, broad peaks of 105 and 113 eV and at 1400 °C, broad peaks of 104 and 112 eV, indicating nitrogen atom and oxygen atom both bonded to silicon atom in the case of [SiN₃O]. At 1500 °C, peak at 103 eV corresponds to nitrogen atom bonded to silicon atom in the case of [SiN₄]. Compared with the intensity of peak at 1400 °C, the intensity of peak at 1000 °C is weaker, indicating that there is no Si₂N₂O and Si₃N₄ phases separation in the SiCON ceramic matrix. In the EELS spectra of the N–K-edge, at 1000 and 1400 °C, the broad peak at 405 eV can be assigned to [SiN₃O] unit. At 1500 °C, the broad peak at 405 eV is due to [SiN₄] unit. In the EELS spectra of the O–K-edge, at 1000 and 1400 °C, the broad peak at 542 eV can be assigned to [SiN₃O] unit. At 1500 °C, the signal at 542 eV is very weak, implying small amount of [SiN₃O] unit and majority of [SiN₄]. Thus, it can be seen that Si₂N₂O/Si₃N₄ phases can be detected between 1000 and 1500 °C and Si₃N₄ phase become the majority in the final ceramic composites with the increase of heating temperature up to 1500 °C. In addition, there is no any [SiC₄] signal existing at 1000–1500 °C, which is consistent with the above-mentioned XRD and TEM results as well as chemical composition analysis.

According to the results of the EELS spectra and XRD patterns, it is ascertained that the single phase of Si₂N₂O that is a promising candidate for high temperature applications owe to their good resistance to oxidation and to thermal shock,

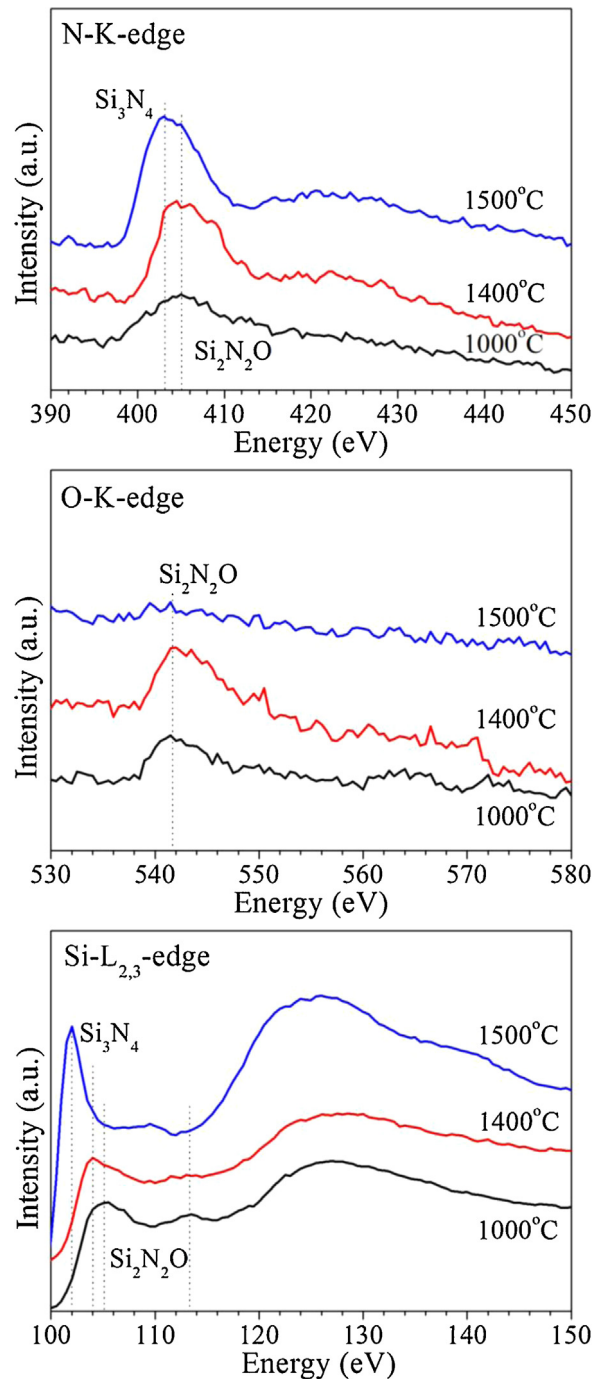


Fig. 11. EELS of Si–L_{2,3}-edge (a), N–K-edge (b) and O–K-edge (c) for the as-prepared SiCON ceramics at 1000, 1400 and 1500 °C.

was formed at 1000 °C. Furthermore, with increasing the heating temperature, the weight percentage of Si₂N₂O phase was decreased while the content of α-Si₃N₄ phase was increased in the composites. In addition, it is very interesting that the residual carbon in Si₂N₂O/α-Si₃N₄ these composites disappeared after the heat-treatment temperature of 1500 °C, which is ascribed to the formation of Si₂N₂O phase. However, these carbon species still remains in the composites using the non-oxygen chlorosilane precursor under the same experimental condition.^{7,9,29} Si-NMR and ¹³C-NMR spectra of ceramics are

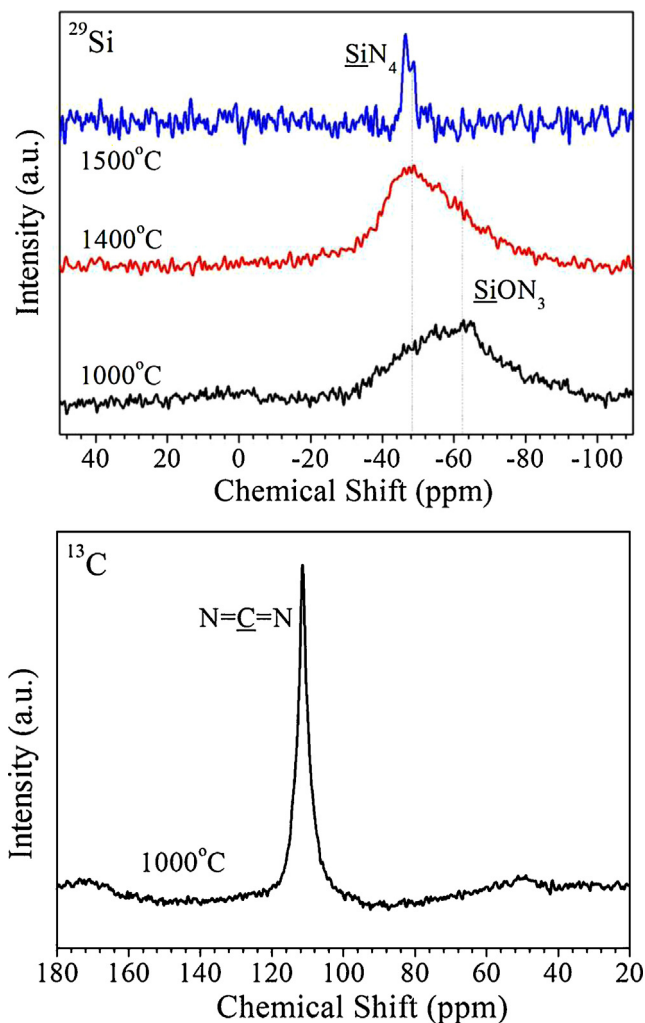


Fig. 12. ^{29}Si (a) and ^{13}C (b) NMR spectra of the as-prepared ceramics at 1000, 1400 and 1500 °C.

shown in Fig. 12. It can be observed that the main composition of ceramics consists of $\text{Si}_2\text{N}_2\text{O}/\text{Si}_3\text{N}_4$ at 1000–1500 °C while the major phase of the composites is Si_3N_4 at 1500 °C. The ^{29}Si -NMR spectrum of the ceramic at 1000 °C is characterized by a broad peak centered at about -62 ppm (-40 to -80 ppm), which is assigned to $[\text{SiN}_3\text{O}]$ and $[\text{SiN}_4]$ units.²⁷ At 1400 °C, a broad peak centered at -49 ppm, characteristic of $\sim 50\%$ $\text{Si}_2\text{N}_2\text{O}$ and $\sim 50\%$ Si_3N_4 . At 1500 °C, a sharp signal at -49 ppm, indicating the main Si_3N_4 phase.^{28–30}

In order to trace the existence of free carbon in the composites, the ^{13}C -NMR spectra of as-prepared samples were presented. The ^{13}C -NMR spectrum at 1000 °C shows a peak centered at about 110 ppm for $[\text{N}=\text{C}=\text{N}]$ band. Corresponding to the results by chemical elemental analysis and FT-IR, $\text{SiOSiN}_2(\text{NCN})$ is the structure of the ceramic. It is different from ceramics derived from PSCN precursors, in which the $[\text{N}=\text{C}=\text{N}]$ unit is usually less intense and occurs at around 120–124 ppm.^{27,31} Above 1000 °C, no carbon signal can be detected. Compared to the previous works,^{7–15} it is interesting that residual carbon in the ceramic composite nearly disappeared and no SiC phase was observed in the final $\text{Si}_2\text{N}_2\text{O}/\text{Si}_3\text{N}_4$ composite after

post-pyrolysis heat treatment above 1000 °C. Thus, the in situ chemical synthesis via the thermolysis of the novel polysilyloxy-carbodiimide precursors in this work could successfully produce the perfect $\text{Si}_2\text{N}_2\text{O}/\text{Si}_3\text{N}_4$ composite ceramics that are promising candidates as porous ceramic materials for a broad range of engineering applications, demanding high strength, low density, high surface area, high permeability, low specific heat and high thermal insulation.

4. Conclusions

In this work, in situ chemical synthesis of $\text{Si}_2\text{N}_2\text{O}/\text{Si}_3\text{N}_4$ composite ceramics was fabricated via the thermolysis of novel polysilyloxy-carbodiimide ($[\text{SiOSi}(\text{NCN})_3]_n$) precursors between 1000 and 1500 °C in nitrogen atmosphere. The relative structures of $\text{Si}_2\text{N}_2\text{O}/\text{Si}_3\text{N}_4$ composite ceramics can be explained by the structural evolution observed by electron energy-loss spectroscopy but also by Fourier transform infrared and ^{29}Si -NMR spectrometry. The polysilyloxy-carbodiimide precursor was applied for the controllable insert of oxygen into ternary SiCN structure. The existence of oxygen in the ceramic matrix offers a ceramic composite structure with $\text{Si}_2\text{N}_2\text{O}$, Si_3N_4 and free carbon phases and results in the decrease of carbon in the system, accompanying with tunable composition of $\text{Si}_2\text{N}_2\text{O}/\text{Si}_3\text{N}_4$ composite materials. Especially, the amorphous $\text{SiN}_{1.80}\text{C}_{1.16}\text{O}_{0.47}$ ceramic with a porous structure was obtained via a pyrolyzed process at 1000 °C. After heat-treatment at 1400 °C, it was found that the amorphous SiCN composite ceramics were composed of 53.2 wt.% $\text{Si}_2\text{N}_2\text{O}$ and 46.8 wt.% Si_3N_4 phases. Furthermore, the amount of amorphous $\text{Si}_2\text{N}_2\text{O}$ phase decreased gradually after heat-treatment at 1500 °C. The final crystalline products consisted with 12.8 wt.% $\text{Si}_2\text{N}_2\text{O}$ and 87.2 wt.% Si_3N_4 phases. In addition, the amount of carbon nearly decreased to zero and no SiC phase was observed in the final materials. Thus, it is feasible to the direct synthesis of $\text{Si}_2\text{N}_2\text{O}/\text{Si}_3\text{N}_4$ composite materials with tunable compositions and porous structures via facile thermal process of PDC materials that can be effectively controlled by the design and synthesis of organosilicon precursors.

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