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The influence of pyrolysis temperature on the oxidation resistance of carbon-rich SiCN ceramics derived from reaction of silazanes with acrylonitrile

L. Ribeiro^{a,*}, A. Bezerra^b, C. Gervais^c, S. Bernard^d, R. Machado^b, G. Motz^{e,*}

^a Federal University of Santa Catarina, 88905-120, Araranguá, Brazil

^b Federal University of Santa Catarina, 88040-900, Florianópolis, Brazil

^c Sorbonne Universités, UPMC Univ Paris 06, 75005, Paris, France

^d Univ. Limoges, CNRS, IRCER, UMR 7315, F-87000, Limoges, France

^e University of Bayreuth, D-95447, Bayreuth, Germany

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ABSTRACT

The influence of pyrolysis temperature on the oxidation resistance of carbon-rich SiCN ceramics derived from reaction of acrylonitrile with a commercially available oligosilazane (HTT1800) and its subsequent pyrolysis in nitrogen atmosphere was evaluated. The investigation of the oxidation behavior reveals that the final pyrolysis temperature plays an important role in the oxidation resistance of the developed SiCN/C nanocomposites. Increasing the pyrolysis temperature promotes an ordering of the free-carbon phase and consequently, an improvement of the oxidation resistance is noticed. However, starting phase separation during annealing at 1500 °C reduces slightly the protection effect provided by the oxidation resistant Si₃N₄ phase.

1. Introduction

Manufacturing of silicon-based ceramics via polymer-derived ceramics (PDCs) route presents several benefits over the conventional ceramic processing from powders. The major advantages of PDCs technology are the relatively low processing temperatures and the applicability of well-established polymer processing techniques [1]. Moreover, the phase composition and nanostructure in PDCs can be adjusted by the manipulation of chemistry and molecular architecture of the polymeric precursor, which allows designing preceramic polymers to obtain ceramics with tailor-made properties [2].

Ceramics in the ternary Si-C-N system processed via the PDC route are of great interest due their high oxidation and temperature stability [3–5]. Polyorganosilazanes and polysilylcarbodiimides are the main polymeric precursors used to process Si-C-N ceramics and offer the advantage to modulate their phase composition. Hence, the pyrolysis of polyorganosilazanes up to 1000 °C in protective atmosphere leads to an amorphous ceramic mostly composed of various Si_xN_{4-x} (0 ≤ x ≤ 4)-type environments and segregated carbon phase (so-called free-carbon) [6–9]. In contrast, the pyrolysis of polysilylcarbodiimides at the same conditions yields mainly amorphous Si₃N₄ and free-carbon

[10,11].

The incorporation of free-carbon in the aforementioned ceramics is very interesting to influence their properties. Free-carbon formation starts at temperatures around 600 °C, when the rupture of hydrocarbon groups bonded to silicon leads at first to condensed aromatic carbon structures. With increasing temperature, residual hydrogen bonded to carbon evolves leading to a further aggregation and separation by forming an amorphous network with a graphite-like structure at the end [6,12–15].

The amount of free-carbon plays an important role in the thermal stability of PDCs. Recent studies showed interesting application for carbon-rich SiCN ceramics as a very efficient alternative to carbon in lithium-ion battery [16–19] and also as a very robust catalyst support [20,21]. Moreover, carbon-rich PDCs are more resistant against crystallization and decomposition in comparison to their low-carbon analogues [11,22]. However, their oxidation resistance tends to decrease as the free-carbon content increase.

In general, the development of carbon-rich PDCs follows three strategies: (i) synthesis of preceramic polymers with a high content of suitable organic groups; (ii) addition of carbon powder to a preceramic polymer; (iii) the use of carbon precursors in combination with

2. Experimental

2.1. Processing of the C-rich SiCN ceramics

The oligosilazane HTT1800 (commercially available as Durazane 1800, Merck KGaA, Germany) was selected as the SiCN ceramic precursor and acrylonitrile (Sigma Aldrich, Germany) was used as the polyacrylonitrile (PAN) forming monomer. The simplified chemical structures of the oligosilazane and acrylonitrile are shown in Fig. 1.

Hybrid polymers were prepared via free-radical solution polymerization using the same procedure described elsewhere [27]. Azobisisobutyronitrile (AIBN) was used as initiator and dimethylformamide (DMF) as a solvent, both acquired from Sigma Aldrich (Germany). The amount of solvent was set to 80 wt.% and the amount of initiator was fixed at a ratio of 0.015 mol/mol of the available vinyl groups. Four hybrid compositions were prepared, in addition to the pure compounds which were also polymerized under the same conditions. The sample

designation and their respective compositions are presented in Table 1.

After the polymerization reaction, the solvent was removed under reduced pressure and the samples were pyrolyzed under flowing nitrogen atmosphere. About 1 g of the respective polymer was placed in a carbon crucible and heated up to 1500 °C using heating rate of 5 K/min and kept at this temperature for 1 h. Samples are denoted in the text followed by its final pyrolysis temperature.

2.2. Characterizations

The chemical composition of the pyrolyzed products was quantified by elemental analysis. The carbon content was determined by a combustion analysis with a carbon analyzer Leco C-200 and the nitrogen and oxygen content by hot gas extraction with a Leco TC-436 N/O analyzer (Leco Corporation, Michigan, USA). The silicon content was calculated as the difference of the abovementioned elements to 100 %.

Solid-state ^{29}Si MAS NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (Bruker Corporation, USA) (B_0 7.0 T, $\nu_0(^1\text{H})$ 300.29 MHz, $\nu_0(^{29}\text{Si})$ 59.66 MHz) using 7 mm Bruker probe and a spinning frequency of 5 kHz. Single pulse ^{29}Si NMR MAS spectra were recorded with a recycle delay of 60 s. Chemical shift values were referenced to tetramethylsilane for ^{13}C and ^{29}Si .

X-ray diffraction (XRD) analysis was used to identify the crystallographic nature of the pyrolyzed products. Samples were ground and the resulting powders ($< 75 \mu\text{m}$) were characterized in a D8 ADVANCE XRD equipment (Bruker AXS, Germany) using monochromatic $\text{CuK}\alpha$ radiation to identify crystalline phases.

To investigate the morphology and to identify the phase formation of the pyrolyzed products, transmission electron microscopy (TEM) was performed using a JEM-1011 TEM equipment (JEOL Corporation, Japan) operating at an acceleration voltage of 100 kV. For the sample preparation, the pyrolyzed materials were ground and sieved. The resulting powders ($< 20 \mu\text{m}$) were dispersed in an ultrasonic bath (high purity ethanol 99.8 %, Sigma–Aldrich Co.) and a small droplet of the suspension was placed on a carbon (Cu) grid.

The oxidation tests were performed in the thermogravimetric stability.

preceramic polymers.

In the first case, the amount of free-carbon after pyrolysis can be increased by the incorporation of cross-linkable unsaturated carbon groups with lower hydrogen content in the molecular structure of the precursor. The replacement of e.g. methyl groups bonded to silicon for vinyl groups leads to a ceramic with higher carbon content [23]. However, as reported in many publications, it is nearly impossible that the free-carbon content of SiCN ceramics derived from vinylsilazanes exceeds 30 wt.% [7,14,23,24]. Another strategy was reported by Mera et al. [11]. The authors synthesized carbon-rich phenyl- polysilylcarbodiimides and obtained SiCN ceramics with a carbon content higher than 50 wt.%. The carbon-rich ceramics possess enhanced thermal stability, with respect to crystallization and delayed carbon-thermal reaction.

The other alternatives, including the use of carbon powder and/or a carbon precursor, have been investigated regarding the electrical properties. Graczyk-Zajac et al. [25] reported the processing of composite materials based on a commercial oligosilazane mixed with

graphite powder. By using a different approach, Winamowska et al. [26] increased the carbon content of SiCN ceramics by using potato starch as a carbon precursor in combination with the same oligosilazane. Although in both cases the authors obtain a homogeneous material for potential use in lithium-ion batteries, the formed carbon phase is only micro-dispersed within the resulting pyrolyzed composite material. Apparently, the use of simple mixtures or blends of the components without interactions at the molecular level does not lead to the formation of a homogeneous material with a well-distributed carbon phase after pyrolysis.

Recently, we reported about the synthesis of a novel hybrid polymer based on polyacrylonitrile (PAN) and a commercially available oligosilazane (ML33) to process carbon-based fibers with strongly enhanced oxidation resistance [27]. Depending on the composition used, the pyrolysis in N_2 atmosphere of this hybrid polymer leads to the formation of amorphous $\text{C}/\text{Si}_3\text{N}_4$ nanocomposites with well-distributed phases, even at temperatures up to 1500 °C. This strategy would be also an interesting alternative to design PDCs with a controlled amount of free-carbon.

Compared to other carbon forming organic polymers, acrylonitrile and PAN have decisive advantages. Both are compatible with silazanes, i.e. they show no unwanted reactions with silazanes and enable easy mixing. The latent functional groups can be activated during *in-situ* radical polymerization using initiators to form a homogeneous copolymer and afterwards a highly cross-linked thermoset. Furthermore, the intermolecular interactions avoid the separation of the educts and consequently resulting in a homogeneous material after pyrolysis with a high carbon content. PAN is free of oxygen, which would limit the high-temperature stability of the resulting C-rich ceramic and contains only elements (C,N,H) already present in the silazane. Additionally, acrylonitrile and PAN are cheap, commercially available products and are widely used in industry.

Based on the proven strategy mentioned above, in the present work various carbon-rich SiCN ceramics were synthesized by the *in-situ* free-radical polymerization of acrylonitrile with the commercially available

oligosilazane HTT1800. This oligosilazane was chosen as the vinyl groups should enhance both the reaction with acrylonitrile and the cross-linking behavior of the reactants. Such are the preconditions for the formation of a very homogeneous C/SiCN material during pyrolysis in nitrogen atmosphere, which finally leads to an improved oxidation resistance at higher temperatures. As this approach allowed for the control and the tailoring of the carbon content, the development of the microstructure and the oxidation resistance based on the amount of carbon and on the annealing temperatures were investigated in detail.

The knowledge gained makes an important contribution to the search for materials that are suitable for applications as very robust support of catalysts in electrolyzers or fuel cells, metal-air batteries, as well as processing of carbon fibers and matrices with outstanding oxidation

Netsch STA 449 F3 Jupiter equipment (Netsch GmbH, Germany). Samples of approximately 15 mg were heated from 30 to 1000 °C with a heating rate of 5 K/min using synthetic air as the carrier gas.

3. Results and discussion

3.1. Investigation of the ceramic phase formation up to 1000 °C

The elemental composition of the samples pyrolyzed up to 1000 °C in nitrogen atmosphere are given in [Table 2](#). The amount of silicon was calculated as the difference to all other elements. Hydrogen was considered to be insignificant and free-carbon was calculated as described in the literature [[28](#)].

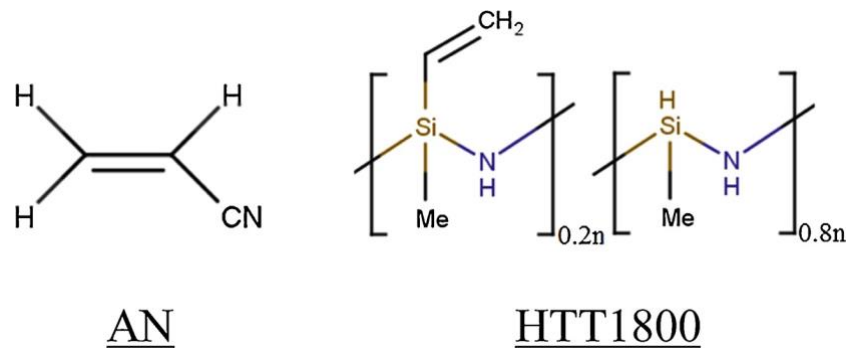


Fig. 1. Chemical structure of acrylonitrile (AN) and HTT1800.

Table 1
Samples compositions.

Sample	Composition (wt.%)	
	HTT1800	AN
PAN	–	100
HTT1800	100	–
H_15	85	15
H_25	75	25
H_40	60	40
H_70	30	70

Table 2
Elemental compositions of samples after pyrolysis at 1000 °C in nitrogen atmosphere.

Sample	Composition (at%)				C _{Free} (wt.%)	Empirical formula normalized on silicon
	Si ^a	C	N	O		
PAN	–	91.1	8.9	0	–	–
HTT1800	38.1	28.4	30.9	2.6	9.5	SiC _{0.75} N _{0.81} O _{0.07}
H_15	35.2	29.8	31.8	3.3	13.2	SiC _{0.85} N _{0.91} O _{0.09}
H_25	31.2	34.2	30.9	3.6	19.0	SiC _{1.10} N _{0.99} O _{0.12}
H_40	24.4	43.0	28.8	3.8	30.4	SiC _{1.76} N _{1.18} O _{0.16}
H_70	11.3	65.8	12.3	10.5	54.5	SiC _{5.82} N _{1.09} O _{0.93}

^a Silicon was calculated as the difference to other measured elements. The amount of hydrogen was considered to be insignificant.

It should be noted that all pyrolyzed samples presented undesirable oxygen contamination due to water impurities present in DMF [27].

As expected, the carbon content is increased with the incorporation of PAN. But also that the amount of the formed free-carbon is directly dependent on the acrylonitrile concentration in the starting reaction mixture. An important implication of these results is the possibility to design carbon-rich PDCs with the desired amount of carbon by simply adjusting the acrylonitrile:silazane ratio during synthesis, which represents a simpler approach compared to the chemical modification of the polymeric precursor.

Regarding the nitrogen content, it is noteworthy to mention that the Si/N ratio increases with the increase of the PAN content. Excluding samples with high oxygen contamination (H_70), where any interpretation could lead to wrong conclusions since oxygen replace nitrogen, it would be expected that the nitrogen content decreases with increasing PAN amounts. Once pure PAN provides less nitrogen than the silazanes any composition of PAN with silazanes should lead to a ceramic material with an intermediate amount of nitrogen if there is no interaction between the two components. The excess of nitrogen found could be explained by the crosslinking reactions between the Si-H groups from silazane with the N-functionalities of PAN, as was demonstrated in our

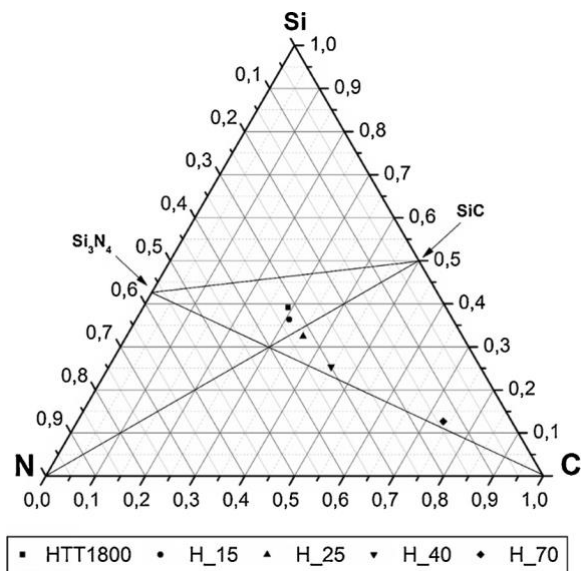


Fig. 2. Ternary Si-C-N phase diagram with the molar compositions of the SiCN

ceramics. Hydrogen and oxygen were neglected. The diagram is arranged clockwise.

previous investigation [27].

The elemental composition is also displayed in the ternary SiCN diagram with the molar compositions of the pyrolyzed samples (Fig. 2).

As displayed in Fig. 2, the resulting ceramic composition of samples synthesized with more than 40 % of acrylonitrile tend to lie on the tie-line between Si_3N_4 and carbon, indicating that both phases dominate the sample composition. This behavior indicated that, besides the increase in the carbon content, the incorporation of PAN also influences the ceramic phase formation. Comparing the solid state ^{29}Si NMR spectra of sample HTT1800 (1000 °C) with H_40 (1000 °C) (Fig. 3), the difference in the ceramic phase composition is obvious. In contrast to the sample HTT1800 (1000 °C), where various $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 2$) are detected, the formation of SiN_4 sites is preferred for sample H_40 (1000 °C). This behavior is attributed to the aforementioned crosslinking reaction during pyrolysis. The increasing amount of PAN leads to an increased number of new Si-N bonds and consequently favor the formation of the Si_3N_4 phase.

3.2. Investigation of the ceramic phase formation up to 1500 °C

Because all samples pyrolyzed up to 1300 °C are X-ray amorphous, only the XRD spectra of samples pyrolyzed at 1500 °C are shown (Fig. 4). The formation of the $\alpha\text{-Si}_3\text{N}_4$ crystalline phase was detected for samples synthesized with up to 25 wt.% of acrylonitrile (based on Powder Diffraction File N° 40-1129, ICDD). In case of the samples with low carbon content, phase separation in the amorphous SiCN phase starts at temperatures higher than 1400 °C, leading to the formation of Si_3N_4 crystallites [10,30]. Interestingly, hybrid compositions

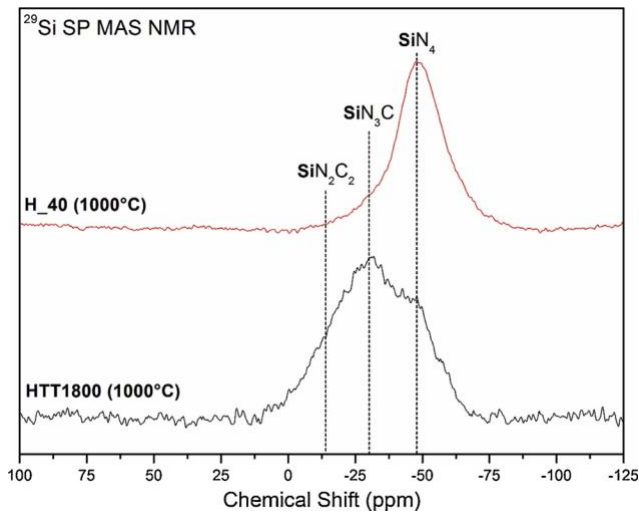


Fig. 3. Solid-state ^{29}Si SP MAS NMR spectra of samples HTT1800 and H_40 heat-treated at 1000 °C in N_2 atmosphere. The $\text{SiC}_n\text{N}_{n-4}$ ($0 \leq n \leq 2$) environments are assigned as reported in the literature [8,9,29].

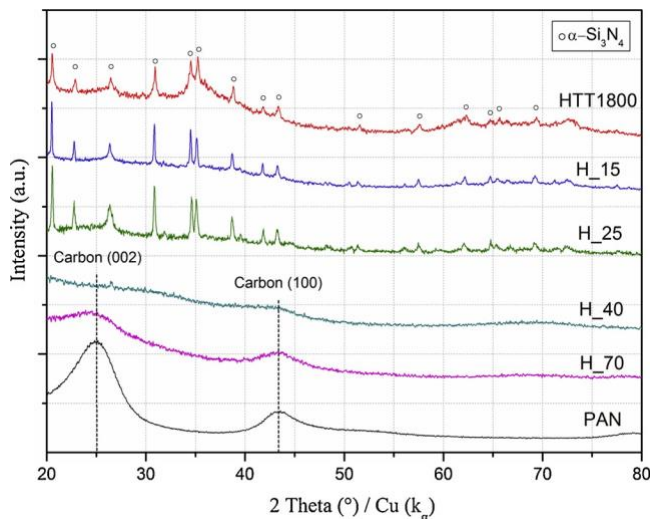


Fig. 4. XRD measurement of samples heat-treated at 1500 °C in N_2 atmosphere.

synthesized with more than 40 wt.% of acrylonitrile also pyrolyzed at 1500 °C are still X-ray amorphous. The higher amount of well-distributed free-carbon phase present in these samples stabilizes

the amorphous ceramic state and avoids the crystallization of Si_3N_4 [10, 11]. However, the formation of Si_3N_4 nanocrystallites, which are not detectable by XRD measurements, cannot be excluded.

In order to obtain more information regarding the nanostructure formation, TEM measurements were performed. Samples synthesized with 25 and 40 wt.% of acrylonitrile were selected for TEM investigations due to the differences in their crystallinity detected by XRD measurements. Fig. 5a shows the TEM micrographs for sample H_25 (1500 °C). The selected area diffraction (SAED) analysis of H_25 (1500 °C) sample (inset Fig. 5a) reveals the presence of crystalline structures assigned to $\alpha\text{-Si}_3\text{N}_4$ phase (based on Powder Diffraction File N° 40-1129, ICDD), also detected through the XRD investigations.

In the case of sample H_40 (1500 °C), also the TEM investigation confirmed the mainly amorphous nature of the sample (Fig. 5b). The corresponding SAED pattern (inset Fig. 5b) exhibit a diffuse ring characteristic for an amorphous material. However, it is important to note that a few smaller crystallites were sometimes observed. An example is given in Fig. 6. The SAED pattern (Fig. 6b) of the corresponding micrograph of sample H_40 (1500 °C) (Fig. 6a) shows the presence of some bright spots in the same region corresponding to the $\alpha\text{-Si}_3\text{N}_4$ pattern. The presence of isolated bright spots instead of rings in the SAED pattern indicates the formation of crystallites in a low concentration. In Fig. 6c the region containing the nanocrystallites (~ 100 nm) is highlighted. The low size and concentration of Si_3N_4 nanocrystallites is the reason that this phase was not detected by XRD studies.

3.3. Oxidation resistance

The oxidation tests of the pyrolyzed samples were performed in a thermogravimetric equipment using synthetic air flow. At first, samples pyrolyzed up to 1000 °C and subsequently oxidized were investigated (Fig. 7). As expected, sample PAN (1000 °C) presents low oxidation resistance at temperatures superior to 500 °C. In contrast, the SiCN ceramic derived from the HTT1800 precursor is completely stable up to 1000 °C. The protection of SiCN ceramics from oxidation is due to the formation of a double $\text{Si}_2\text{N}_2\text{O}/\text{SiO}_2$ passivating layer, which acts as a very effective barrier to the oxygen diffusion [31–33].

The oxidation resistance of the samples H_25 (1000 °C), H_40 (1000 °C) and H_70 (1000 °C), depends on the amount of the ceramic phase. With an increase in the amount of the ceramic phase, the begin of the oxidation is gradually shifted to higher temperatures, revealing the protection effect provided by the well-distributed ceramic phase. But also sample H_70 (1000 °C) with the highest carbon amount possess a remarkably improved oxidation resistance.

To investigate the influence of the final pyrolysis temperature on the oxidation behavior, the samples were also pyrolyzed at 1300 and 1500 °C and subsequently oxidized (Fig. 8). Already the PAN-based carbon sample (Fig. 8a) exhibits a direct relation between the oxidation

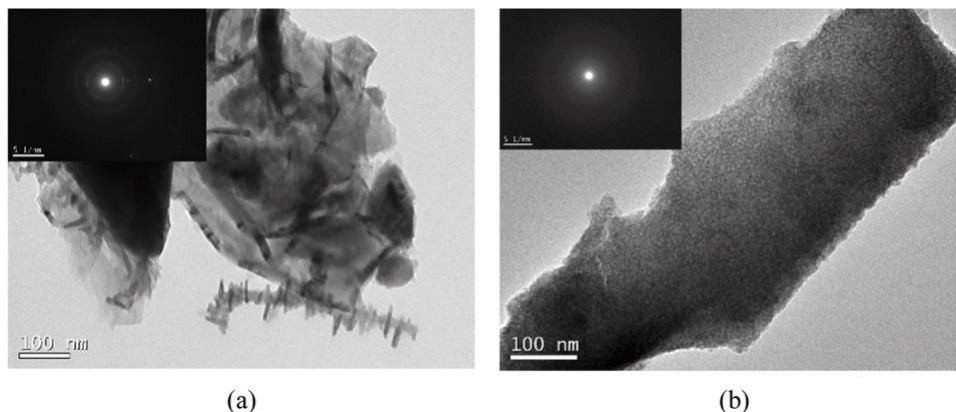


Fig. 5. TEM micrographs of samples (a) H_25 (1500 °C) and (b) H_40 (1500 °C). Inset figures show the corresponding SAED pattern.

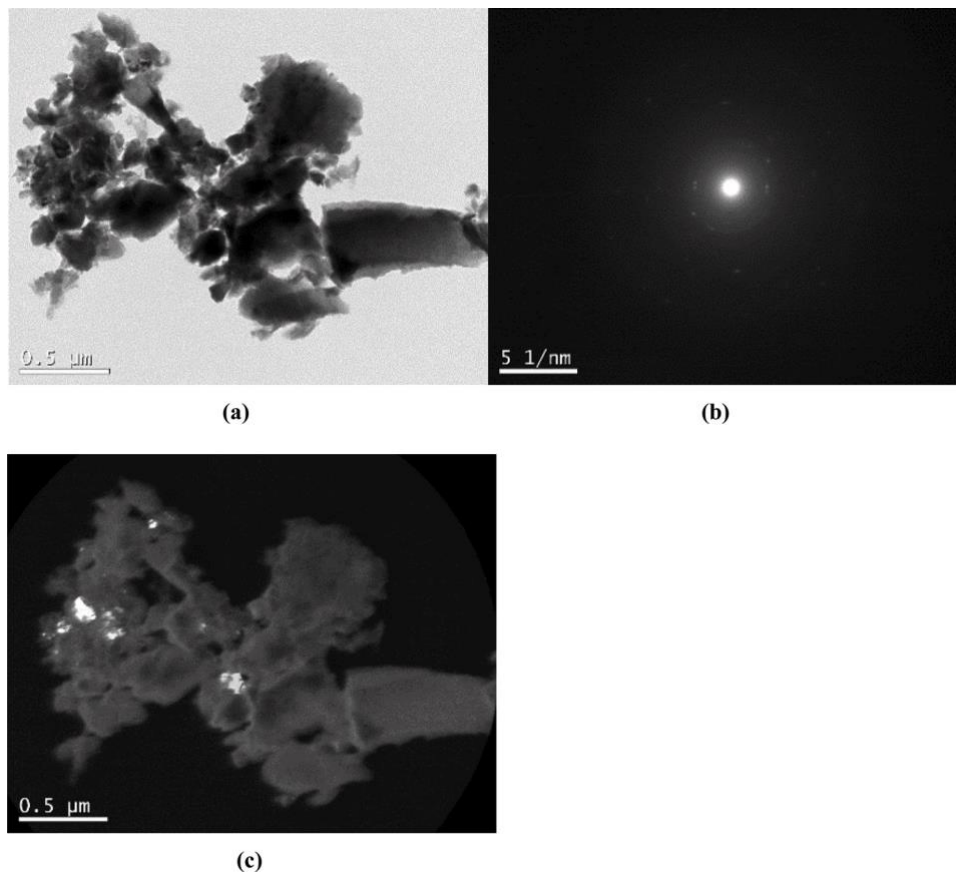


Fig. 6. Formation of nanocrystallites in sample H₄₀ (1500 °C): (a) TEM micrograph, (b) corresponding SAED pattern and (c) TEM micrograph highlighting the location of the Si₃N₄ nanocrystallites.

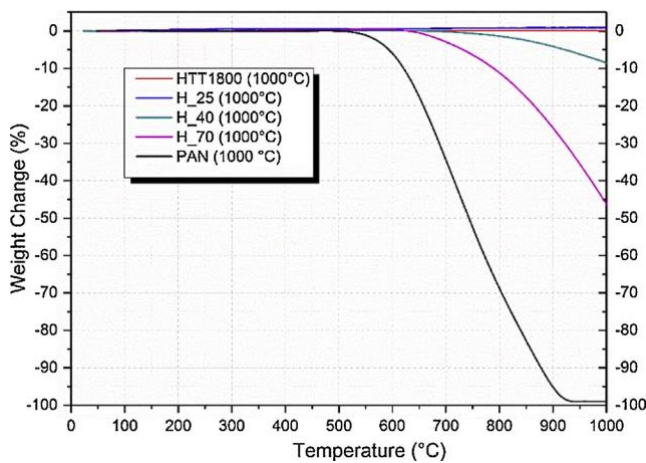


Fig. 7. Oxidation experiments via thermogravimetric analyses of PAN, HTT1800, H₂₅, H₄₀ and H₇₀ samples pyrolyzed at 1000 °C. (heating rate: 5 k min⁻¹; atmosphere: synthetic air).

resistance and the final pyrolysis temperature. An increase of the final heat treatment from 1000 to 1500 °C leads to a delayed start of the oxidation (from 500 to 600 °C). To explain the observed result it is necessary to understand the kinetic mechanisms ruling the carbon oxidation. In the temperature region between 500 and 800 °C, the reaction of carbon with oxygen is not uniform but selective. The oxidation is preferably initiated at some active sites, such as the edges or defects of the carbon layers, which are much more reactive than the carbon in the basal plane [34]. Therefore, the rate of oxidation is directly dependent

on the number of active sites. As the pyrolysis temperature increases, an ordering of the graphite-like structure occurs, thus reducing the number of active sites and consequently decreasing the oxidation rate.

The carbon-rich ceramic derived from sample H₇₀ (Fig. 8b) exhibits the same tendency. The oxidation is strongly reduced after treatment at higher temperatures. The oxidation behavior of sample H₇₀ (1500 °C) is comparable to that of sample H₄₀ (1000 °C), although the free-carbon content is more than 20 wt.% higher. The aforementioned increased ordering of the free-carbon phase associated with the oxidation protection provided by the Si₃N₄ phase leads to this remarkable behavior.

The explanation of the oxidation behavior in dependency on the pyrolysis temperature of the samples H₄₀ (Fig. 8c) is more complicated. As expected, the oxidation resistance increases from sample H₄₀ (1000 °C) to H₄₀ (1300 °C). In fact, sample H₄₀ (1300 °C) presents an outstanding oxidation stability, comparable to pure SiCN ceramics. However, if sample H₄₀ is heat treated up to 1500 °C a slight decrease in the oxidation stability occurred. This behavior may be attributed to the segregation of free-carbon/Si₃N₄ phases also reported for carbon

rich SiCN ceramic [35] leading to increased regions of both phases, which is also a precondition for crystallization. The detection of Si₃N₄ nanocrystallites for sample H₄₀ (1500 °C) via TEM analysis is an evidence for our assumption. The simultaneously formed larger regions of unprotected free-carbon at the sample surface leads to the slightly increased mass loss during oxidation. However, it is important to note that the formation of higher ordered structures (carbon as well as Si₃N₄) compensate this effect and sample H₄₀ (1500 °C) still present a remarkable oxidation stability.

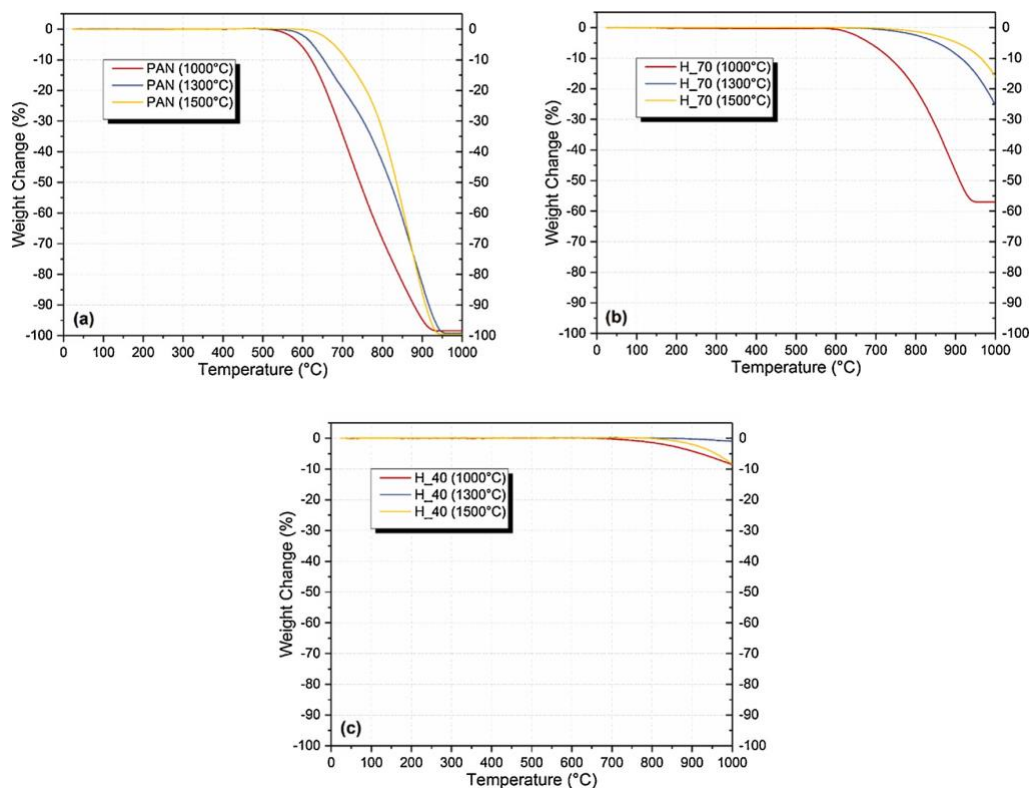


Fig. 8. Influence of the pyrolysis temperature in the oxidation resistance of samples (a) PAN (1000 °C), PAN (1300 °C), and PAN (1500 °C), (b) H₇₀ (1000 °C), H₇₀ (1300 °C), and H₇₀ (1500 °C), and (c) H₄₀ (1000 °C), H₄₀ (1300 °C), and H₄₀ (1500 °C). (heating rate: 5 k min⁻¹; atmosphere: synthetic air).

4. Conclusions

In this work, a new approach to design carbon-rich SiCN ceramics was developed by the *in-situ* free-radical polymerization of acrylonitrile with a commercially available oligosilazane (HTT1800) and its subsequent pyrolysis in nitrogen atmosphere.

Elemental analysis revealed that the free-carbon content of the resulting ceramic depends on the hybrid polymer composition and can be conveniently controlled by simply adjusting the educts ratio during the synthesis.

The PAN content in the hybrid polymer also influences the ceramic phase formation up to 1000 °C. With the increasing amount of acrylonitrile during synthesis, the formation of the Si₃N₄ phase is favored instead of different SiC_xN_y environments. This result is basing on the formation of additional Si-N bonds during the crosslinking reactions between the silazanes and PAN. At temperatures up to 1500 °C samples with a higher free-carbon content (>30 wt.%) are X-ray amorphous.

However, the formation of Si₃N₄ nanocrystallites cannot be excluded, as was demonstrated by TEM analysis.

Beside the free-carbon content, the oxidation stability is also influenced by the final pyrolysis temperature. In general, two mechanisms must be considered to understand and predict the oxidation resistance: I

- The ordering process of the free-carbon phase with the increasing temperature; II – Segregation of free-carbon/Si₃N₄ phases at higher temperatures. In the first case, the ordering process of the carbon phase leads to an improvement in the oxidation resistance, whereas in the second case, the phase separation reduces slightly the protection effect provided by the oxidation resistant Si₃N₄ phase due the formation of increased unprotected free-carbon regions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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