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Original Article

Influence of H_2/NH_3 mixtures on the composition of SiCNYO and SiCNAl(O) nanopowders

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Abstract

We performed pyrolysis of SiCNAlH and SiCNYOH nanopowder precursors under a reactive atmosphere ($Ar/NH_3/H_2$) with various compositions of ammonia (NH_3) and dihydrogen (H_2) to diminish C content, which is deleterious for thermal stability and sintering of the powders. This paper continues a previous work on the fabrication of an Si_3N_4/SiC composite without free C by studying the effect of H_2 on the C/N atomic ratio of the powder. We studied the influence of the nature of the gaseous mixture ($Ar/NH_3/H_2$) on the powder composition. Elemental analysis showed that the introduction of H_2 in the pyrolysis atmosphere limited the decomposition of NH_3 and allowed for control of the C/N ratio. This behaviour can be explained by the structural evolution observed by ^{29}Si NMR spectrometry but also by Fourier transform infrared and Raman spectroscopy. An Si_3N_4/SiC composite, with traces of free C, was obtained after post-pyrolysis heat treatment of the powders synthesized with 10 wt.% of H_2 and 25 wt.% NH_3.

Keywords: Powders-gas phase reaction; Nanocomposites; Si_3N_4; SiC; Shaping; Spray-pyrolysis

1. Introduction

Nanopowders are now widely used as single particles, thin films after deposition, or homogeneous 3-D pieces after shaping. In the field of ceramics, such powders are attractive because of their high reactivity, especially for obtaining dense materials. For SiCN ceramics, the use of nanopowders could also confer a ductil behaviour at high temperature.[1]

Previous work showed that nanopowders could achieve a high homogeneity of a multielement system (SiCNAl(O)).[2] Such powders are produced by spray pyrolysis, from an aerosol of a suitable organometallic precursor. Controlling the material composition is difficult because of the gaseous reactions that take place in the hot zone of the pyrolysis furnace and are responsible for the loss of C- and N-containing species. C and N contents must be adjusted to obtain an Si_3N_4/SiC composite without free C but with a non-negligible amount of SiC to obtain good thermo-mechanical properties.[3,4] Recent results indicate that the C/N ratio can be modified by a reactive pyrolysis atmosphere.[5] For the experimental conditions studied, NH_3 introduced during the thermal pyrolysis is insufficient to avoid the formation of free C, whatever the NH_3 amount introduced into the pyrolysis atmosphere. However, for high contents of NH_3, Si atoms seem to be saturated by an environment of N atoms, and the C/N ratio decreases. Therefore, the C presented into the material is not linked to Si and forms graphite after the powders are annealed at high temperature. The powders, containing a high content of free C, show a very low structural organization characterized by groups such as Si–C–N–Si and are thermally unstable.[5] Furthermore, the presence of free C in the Si_3N_4/SiC powders has a deleterious effect on the sintering behaviour.

Several studies of pyrolysis show that C content could be modified by using H_2 as a part of the reactive atmosphere.[6–9] Previous study of polysilazane and polycarbosilane pyrolysis showed that introducing NH_3 into the pyrolysis atmosphere decreased the final C content.[7,10,11] Li *et al.*[12] compared the composition of powders obtained by spray pyrolysis of hexamethyldisilazane (HMDS) under 2 reactive atmospheres, NH_3 and H_2: the presence of H_2 reduced the C rate by releasing carbonaceous species in the form of hydrocarbons.[6,8]

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Pyrolysis under a mixture of NH_3 and H_2 gases seems to be a good way to control the C/N ratio to retain both Si_3N_4 and SiC phases in the final material and simultaneously avoid the deleterious presence of free C. This work investigates the chemical composition and structural evolution of a SiCN system fabricated by spray pyrolysis under an atmosphere combining NH_3 and H_2, used for C removal, with adjustment of the amount of N and C, respectively. In the present study, we used the same organometallic starting precursors, SiCNYOH and SiCNAlH, as those used in previous studies to create SiCNYO and SiCNAl(O) amorphous and ultrafine powders.[2,13] The results presented below focus on the effect of H_2 (combined with NH_3) on the final composition and thermal stability of the as-prepared powders. We aimed to achieve a composition as close as possible to that of Si_3N_4/SiC composites with the lowest amount of free C as possible.

2. Experimental details

2.1. Powder synthesis

The preparation of SiCNYO and SiCNAl(O) nanopowders was described elsewhere.[2,13] The Y precursor was synthesized by dissolving 2 g silylated Y acetate ($Y(O_2C_5SiH_{11})_3$) in 50 mL HMDS [$(CH_3)_6Si_2NH)$],[14] and the SiCNAlH precursor was obtained by reaction between 50 mL HMDS and 1.8 mL trimethylaluminum ($Al(CH_3)_3$).[2] The different precursors were synthesized under flowing Ar (previously purified through $CaSO_4$ [drierite indicator] and P_2O_5. The elemental composition of each precursor is in Table 1.

All pyrolysis experiments were carried out at 1400 °C with a 3-L min^{-1} total gaseous flow rate. Two atmospheres with variable gas contents were used: Ar/NH_3 and Ar/NH_3/H_2, with contents of 5–25% NH_3 and 0–10% H_2. H_2 mixed with Ar, which carries the aerosol from the generator to the furnace, whereas NH_3 was continuously introduced (at 700–800 °C) in the furnace tube by means of an alumina sheath. After pyrolysis, the powders were stored in a glove box under Ar.

2.2. Annealing

The powders must be stable during the sintering step to prevent any drift of composition at high temperature. During the post-treatment, the powders go through important structural modifications. In this work, annealing experiments were performed with the as-pyrolysed SiCNYO and SiCNAl(O) powders to follow the evolution of each batch during annealing.

For SiCNYO powders, the thermal stability was examined by thermogravimetry analysis (TGA, Setaram, setsys evolution) linked to a mass spectrometer (TA instrument SDT 2960). The powders were heated to 1550 °C at a rate of 10 °C min^{-1} under flowing He and kept at this temperature for 2 h.

For SiCNAl(O) powders, treatment of batches involved use of a dynamic gas mixture (N_2/He, 99.999% purity) to compare their behaviour to that obtained in previous work.[5,15] Powders were compacted at room temperature, and the obtained pellets were embedded in the rest of the powder in a glassy C crucible to prevent compositional changes during the annealing treatment. After the sample was introduced into the graphite chamber furnace, the temperature was increased to 1550 °C (with a 2-h holding time) at an average heating rate of 10 °C min^{-1}. A flow of a mixture of high-purity N (20%) and He (80%) was continuously set in the furnace at a flow rate of 6 L h^{-1}. After annealing, the samples were ground for characterization.

2.3. Characterization techniques

The C, N and O compositions of the as-pyrolysed powders were determined by elemental analysis (HORIBA, EMIA type for C and EMGA type for O and N). The C content was analysed by combustion of powders up to 1800 °C under O, and the O content was measured after C and O were combined, with the C of the crucible, in the form of CO/CO_2, analysed above 2000 C. The amount of N was evaluated by fast pyrolysis of the powders to 3000 °C under He in a graphite crucible. To quantify Si, Al and Y content, inductively coupled plasma-atomic emission spectroscopy was used. Fourier transform infrared (FTIR) spectroscopy (Spectrum One FTIR Perkin-Elmer) involved the KBr pellet method.

Several characterizations of samples involved powder X-ray diffraction (XRD; Siemens, D5000, 2θ, Cu Kα1), SEM (Philips XL 30; powders scattered in an ethanol solution, and part of the sample observed on a SEM substrate after solvent evaporation) and specific surface area measurement (Micromeritics: ASAP 2010, BET 8 pts, N_2). The structural aspect of the treated SiCNAl(O) was examined by Raman spectroscopy (Raman Renishaw RM 1000). Solid-state ^{29}Si NMR spectroscopy (Brüker spectrometer, 400 MHz/89 mm, and Brüker Avance 400 [9.4 T] spectrometer) was used to determine the influence of the pyrolysis atmosphere on the evolution of the Si environment.

3. Results and discussion

3.1. As-pyrolysed SiCNYO and SiCNAl(O) powders

3.1.1. Characterization

The morphologic features of the as-pyrolysed SiCNYO and SiCNAl(O) powders were examined by SEM (Figs. 1 and 2).

Table 1
Chemical composition of precursors. HMDS, hexamethyldisilazane; TMA, trimethylaluminum.

Precursors	Composition (wt.%)						
	Si	C	O	N	Y	Al	H
SiCNYOH (HMDS (50 mL) + silylated yttrium acetate (2 g))	34.2	43.9	0.8	9.4	0.9	–	11.6
SiCNAlH (HMDS (50 mL) + TMA (1.8 mL))	32.8	44.9	–	6.7	–	2	12.3

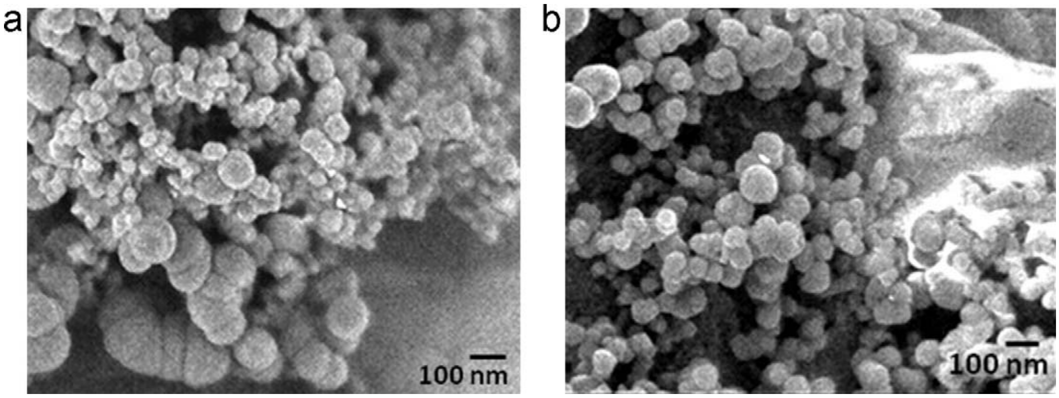


Fig. 1. SEM images of SiCNYO powders synthesized under (a) Ar/NH_3 (75/25%) and (b) Ar/H_2/NH_3 (65/10/25%).

Whatever the pyrolysis atmosphere and molecular structure of the initial precursor, grains exhibited a spherical shape. SiCNYO powders showed a bimodal particle-size distribution (Fig. 1). Moreover, the pyrolysis atmosphere seemed to have a significant effect on the particle-size distribution because of a large granulometric distribution under Ar/NH_3 (75/25%) (20–150 nm) but a narrower granulometric distribution under Ar/H_2/NH_3 (65/10/25%) (50–100 nm).

Contrary to SiCNYO powders, SiCNAl(O) powders showed a monomodal granulometric distribution whatever the pyrolysis atmosphere (Fig. 2). Nevertheless, the particle-size distribution was broad for powders produced without H_2 in the pyrolysis atmosphere (Fig. 2(a)). The diameter was between 10 and 20 nm for the small grains and between 50 and 80 nm for the larger ones. A rather narrow granulometric distribution (70–80 nm) was observed with pyrolysis under Ar/H_2/NH_3 (65/10/25%) (Fig. 2(b)).

We first investigated the variation in atomic composition of the as-prepared SiCNAl(O) powders to determine the working conditions leading to the lowest amount of free C inside the powders before studying the fabrication of SiCNYO powders.

The particle diameters measured by image analysis were confirmed by the specific surface area values and those of the equivalent disc diameter calculated with the density determined by He pycnometry. Table 2 presents the specific surface area, density and values of equivalent disc diameter of the as-pyrolysed SiCNYO powders obtained after pyrolysis at 1400 °C under Ar/NH_3 and Ar/H_2/NH_3. First, the as-fabricated powders were dense because the calculated diameters were consistent with those of the observed particles (Fig. 1). Second, the density of the powders varied slightly with composition of pyrolysis atmosphere. Moreover, in both cases, the density of the powders remained weaker than the theoretical density of SiC (3.22) and Si_3N_4 (3.44). This difference can be explained by the amorphous state of the system.

Examination of the elemental compositions (*i.e.* C/N and Si/N ratios) of the as-pyrolysed SiCNYO and SiCNAl(O) powders ($T_{\text{pyrolysis}} = 1400\,°C$) with and without H_2 in 25% NH_3 was followed by chemical analysis.

For the SiCNYO powders, Table 3 shows a slight increase of the C content (from 9 to 10 wt.%) and a simultaneous decrease of the N content (from 31 to 25 wt.%) with 10% H_2 and 25% NH_3 introduced in the pyrolysis atmosphere. This situation implies an increase in the C/N and Si/N ratios. The Y content was stable at 500 ppm whatever the composition of the reactive atmosphere. As well, the Y rate was lower than that initially introduced in the precursor. To justify the weak Y rate measured in the as-pyrolysed powders, its evolution was studied throughout the pyrolysis process. First, during spraying, the Y content in different samples was reduced with time. Second, the reactional zone was analysed by *Energy Dispersive X-ray Spectroscopy* (EDS) after experiments, but no remaining Y could be detected

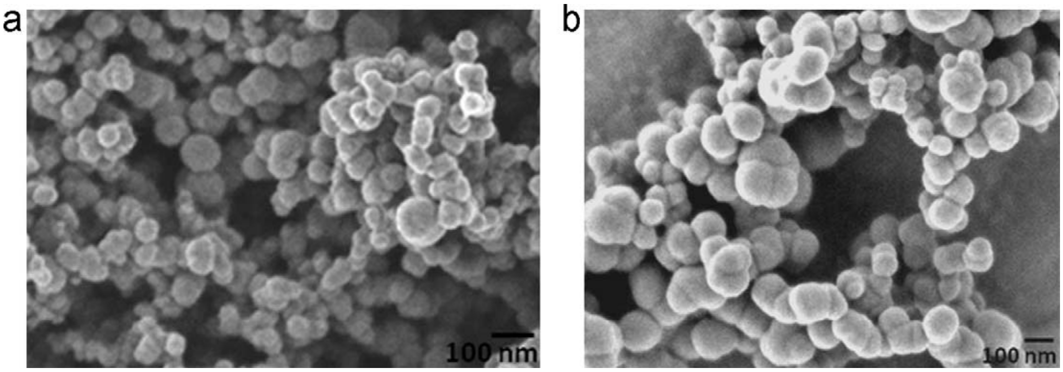


Fig. 2. SEM images of SiCNAl(O) powders synthesized under (a) Ar/NH_3 (75/25%) and (b) Ar/H_2/NH_3 (65/10/25%).

Table 2
Specific surface area, density and particle size of SiCNYO powders.

% Ar	% NH_3	% H_2	Specific surface area ($m^2 g^{-1}$)	Density	Equivalent disc diameter (nm)*
75	25	0%	33.9	2.6	68
65	25	10%	37.4	2.8	57

* d_{eq} (nm) = 6000/($d.S_{BET}$).

Table 3
Elemental composition of SiCNYO powders.

Atmosphere			Chemical composition (wt.%)					Molar ratios	
% Ar	% NH_3	% H_2	C	N	O	Si	Y (ppm)	C/N	Si/N
75	25	0	88	31.0	4.8	53.3	500	0.3	0.8
65	25	10	9.9	28.8	4.0	51.8	500	0.4	0.9

in the furnace tube. The difficulty in dissolving the powders for the chemical analysis relates to the weak Y content. Therefore, the value of 500 ppm Y (Table 3) is thought to be the minimum for each powder batch. We are currently working to solve this problem.

To specify the role of NH_3 and H_2 in the thermal decomposition of the precursors, we investigated the synthesis of SiCNAl(O) powders. Without H_2, the C content decreased from 46% to 3% and the NH_3 rate increased from 0% to 25%, which implies a simultaneous increase of the N amount from 12% to 47% (Table 4). As previously mentioned, we obtained a high N content with 25% NH_3 introduced into the pyrolysis atmosphere. This evolution effect was clearly shown by the C/N and Si/N ratios, which were reduced. The evolution of these elements with various amounts of NH_3 without H_2 was discussed previously.[5] With 10% H_2 introduced into the atmosphere with 5% and 25% NH_3, similar evolutions were noted (decrease in C content and increase in N content). As well, O, Si and Al contents changed with the composition of the reactive atmosphere. The presence of H_2 allows for stabilizing the Al and Si contents and enhances a slight decrease in the O amount.

With 25% NH_3 without H_2, the molar ratio of Si/N = 0.5 implies a N excess in the powders. In contrast, a controlled molar ratio of Si/N = 0.7, which is close to the value (Si/N = 0.75) in the pure Si_3N_4 material, can be achieved with 10% H_2 mixed with 25% NH_3 in the pyrolysis atmosphere.

To further understand the role of H_2, we investigated the evolution of the SiCNAl(O) composition after pyrolysis under Ar/NH_3 and $Ar/NH_3/H_2$, separately. According to the results of Table 4, with the Al content being very low, the theoretical chemical composition of nanopowders can be expressed in a stoichiometric equivalent compound (Table 5). The proportion of free C decreased from 38% to 5% with the amount of NH_3 increased from 0% to 15%.

According to Table 5, powders synthesized with 5%, 15% and 25% NH_3 without H_2 lead to materials rich in Si_3N_4. Indeed, a great part of the Si seems to react preferentially with the N derived from NH_3 to give an Si_3N_4 phase. Consequently, a small amount of Si remains available to form SiC or mixed $SiC_{4-x}N_x$ tetrahedra. In these conditions, the final material would essentially consist of Si_3N_4 and free C, which does not allow for producing the Si_3N_4–SiC composite.

The presence of H_2 must modify the reactivity of NH_3 because a high content of C was detected. As observed in Table 4, the introduction of 10% H_2 to a gas mixture containing 5% NH_3 leads to an increase of C content from 22.5 to 28 wt.% and a decrease in N content from 35 to 24 wt.%. The resulting powder composition is less affected by the C removal and the nitridation phenomena. Fig. 3 summarizes the overall evolution of the powder composition with the nature of the atmosphere (*i.e.* percentage NH_3 and H_2). The presence of H_2 clearly explained the modified C/N ratio, which is difficult to control with an Ar/NH_3 gas mixture. Therefore, this ratio can be controlled more precisely at about 0.2 with 10% H_2 used in a pyrolysis atmosphere containing 25% NH_3. The presence of H_2 disturbs and partially inhibits the reactivity of NH_3 because a high C amount is detected, as well as a low N content. A weak amount of N

Table 4
Elemental composition of SiCNAl(O) powders synthesized with different atmospheric compositions.

Atmosphere			Chemical composition (wt.%)					Molar ratios	
% Ar	% NH_3	% H_2	**C**	N	O	Si	Al	C/N	Si/N
100	0	0	45.8	11.9	0.6	36.6	0.5	4.5	1.5
95	5	0	22.5	34.8	1.5	47.3	1.5	0.7	0.7
85	15	0	46	37.0	5.2	51.6	1.2	0.1	0.7
75	25	0	3.4	46.6	5.1	44.6	0.9	0.1	0.5
85	5	10	28.4	23.9	0.5	49.1	1.4	1.4	1.0
65	25	10	8.6	33.1	1.5	49.1	1.4	0.3	0.7

Table 5
Theoretical composition according to Ar/NH_3 compositions.

Atmosphere		Equivalent composition (wt.%)			Free C	N excess
% Ar	% NH_3	Si_3N_4	SiC	SiO_2		
100	0	29.8	25.4	1.9	38.2	–
95	5	76.5	–	2.8	22.5	3.6
85	15	78.3	–	9.7	4.6	5.6
75	25	66.8	–	9.0	3.4	19.8

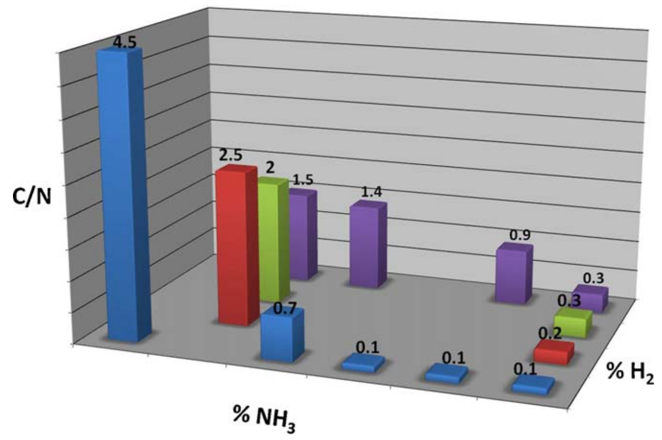


Fig. 3. Evolution of composition of powders by nature of the atmosphere.

is necessary to avoid the formation of C–N, C=N and/or C≡N bonds.[5] As a consequence, some Si atoms should be available to form Si–C bonds, which may limit the formation of free C in the final material and increase its thermal stability, because free C reacts with Si_3N_4 at high temperature, thus leading to an evolution in N content and formation of SiC.

According to these last results, we further focused on powders synthesized with 10% H_2 and 25% NH_3 (Ar/NH_3/H_2 atmosphere). We also compared the structural evolution of SiCNYO and SiCNAl(O) powders synthesized in various atmospheres. Fig. 4 presents FTIR spectra of as-pyrolysed SiCNYO and SiCNAl(O) synthesized in Ar/NH_3 (a) or Ar/NH_3/H_2 (b) mixtures. The broadest and highest band at 900 cm^{-1} from 700 to 1100 cm^{-1} corresponds to Si–N–Si (950 cm^{-1}) and Si–C (870 cm^{-1}) groups in an amorphous SiCN structure.[9,11] Spectra show bands at 2200, 1600 and 1300 cm^{-1}, for C≡N, C=N and C-N, respectively. However, with H_2 in the pyrolysis atmosphere, the band intensities at 2200, 1600 and 1300 cm^{-1} are lowered. Contrary to previous results,[5] nitridation of the as-pyrolysis powders could be limited with 10% H_2 used with 25% NH_3. Therefore, most of the C contained in powders may be linked to Si, with a negligible amount linked to N.

Examination of the structural evolution of powders with reactive atmosphere was followed by ^{29}Si NMR spectroscopy. In this part of the work, we were interested in the influence of the nature of the precursor on the structural arrangement of the SiCN system obtained under similar pyrolysis conditions. ^{29}Si NMR spectra of the as-pyrolysed SiCNYO and SiCNAl(O) powders obtained with 25% NH_3 and 10% H_2 are in Fig. 5. As shown in previous work (pyrolysis under Ar),[2] 3 main environments could be identified, corresponding to C-rich environments ($\underline{Si}C_4$/$\underline{Si}C_3N$) and N-rich environments $\underline{Si}CN_3$ $\underline{Si}N_4$.[16] A global view of each spectrum, presented in Fig. 5, clearly shows different environments of Si for the as-pyrolysed SiCNYO and SiCNAl(O) powders. Nevertheless, both precursors contained same quantity of HMDS. This finding may be due to the different molecular structure of the raw precursors. Especially, in the case of the SiCNYOH precursor, the Y acetate was silylated before its dissolution in HMDS, which could explain the different Si environments in the SiCNYO and SiCNAl(O) powders.[2,14]

For the SiCNYO powders (Fig. 5(a)), the spectrum shows a broad peak from −10 to −60 ppm, with an apex at −50 ppm, which indicates a N-rich environment such as SiN_4. Within this large peak, the resonances at −14, −20 and −37 ppm, are assigned to $\underline{Si}C_3N$, $\underline{Si}C_4$ and $\underline{Si}CN_3$, respectively. Moreover,

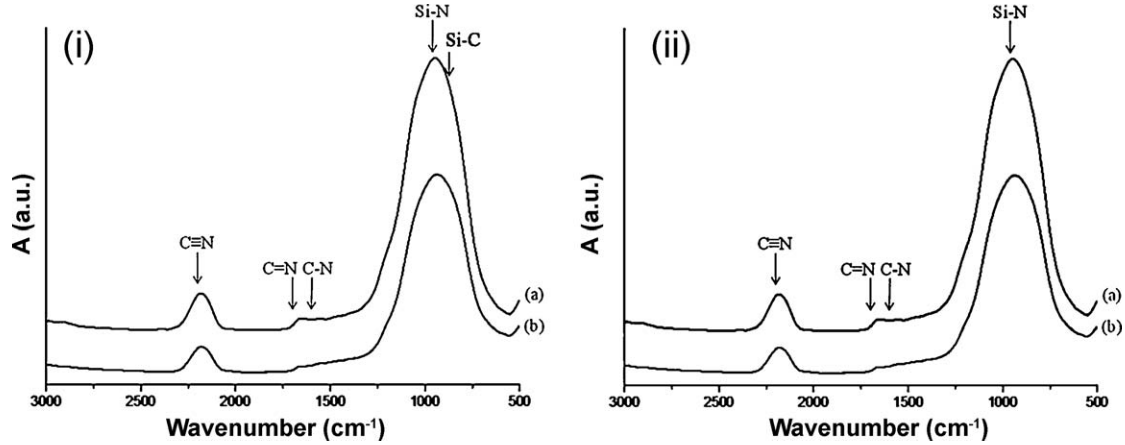


Fig. 4. Fourier transform infrared spectra of the as-synthesized SiCNYO (i) and SiCNAl(O) (ii) powders synthesized under (a) Ar/NH_3 and (b) Ar/NH_3/H_2 (10%).

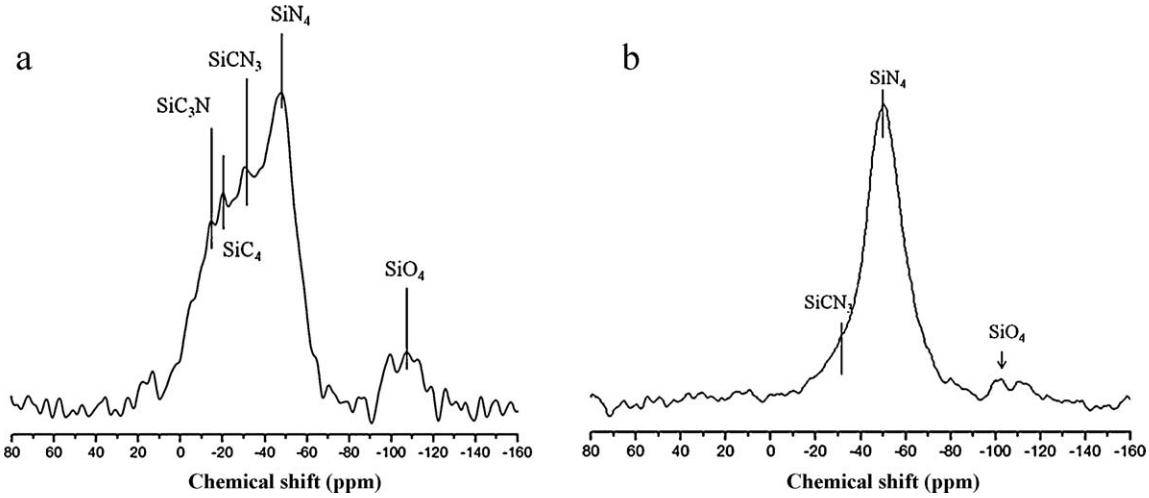


Fig. 5. ^{29}Si solid-state NMR of as-pyrolysed (a) SiCNYO and (b) SiCNAl(O) powders obtained with 10% H_2 and 25% NH_3.

the second broad peak, with low intensity at −110 ppm, corresponds to an $\underline{Si}O_4$ environment and could be assigned to silica or a silicate. For the SiCNAl(O) powders (Fig. 5(b)), N-rich (SiN_4) environments are visible, with the main peak at −50 ppm, and may be assigned to an environment such as $\underline{Si}CN_3$ around −35 ppm.[16]

3.1.2. Discussion

As-pyrolysed SiCNYO and SiCNAl(O) powders are spherical, dense and amorphous, whatever the nature of the precursor and the pyrolysis atmosphere. However, the average particle diameter of the SiCNYO powders is between 20 and 100 nm and that for SiCNAl(O) powders from 70 to 80 nm. SiCNYO powders previously showed a bimodal granulometric distribution that could be due to phenomena during spraying.[13] In these conditions, the SiCNYOH precursor showed the mechanisms of drop-to-particle and gas-to-particle.[13] The thermal spray-pyrolysis of the SiCNAlH precursor forms only droplets, which could explain the monomodal granulometric distribution of SiCNAl(O) powders. As well, the carrier gas composition seems to have a significant effect on the particle-size distribution of the SiCNYO and SiCNAl(O) powders. The granulometric distribution is narrower with 10% H_2 in the pyrolysis atmosphere.

The main difference observed between the powders synthesized with and without H_2 concerns the elemental composition. In this work, we performed pyrolysis experiments in a reactive atmosphere ($Ar/NH_3/H_2$) with different amounts of NH_3 and H_2. The reduction in the C amount in the presence of NH_3 could be explained by the cleavage (by nucleophilic attack) of the Si–C bonds and the release of gaseous species such as CH_4 and C_2H_6. Several studies investigated the different steps of the precursor-to-ceramic conversion with NH_3 used in the reactive atmosphere.[8,17] As previously mentioned, NH_3 is introduced into the furnace between 700 and 800 °C, then it is gradually increased to 1400 °C by passing through the alumina sheath. When the temperature is below 700 °C, molecular NH_3 would react directly with the $–Si^•$ and $–CH_3^•$ radicals created from the decomposition of $Si–CH_3$ at low temperature. Different reactions presented in Scheme 1 suggest that the reduced C content may be due to release of CH_4. In parallel, the increased rate of N may be due to the formation of the $NH_2^•$ radical.

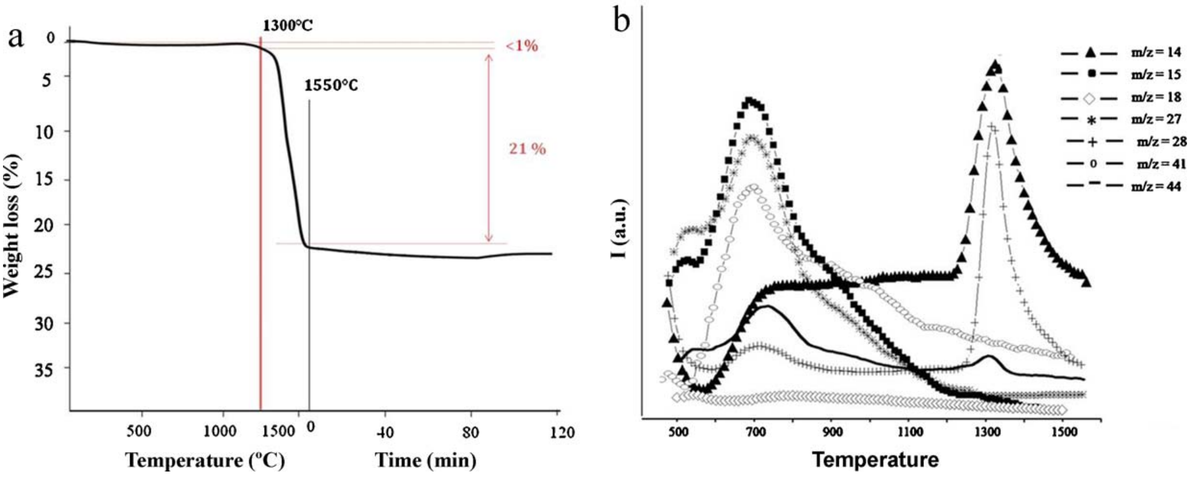
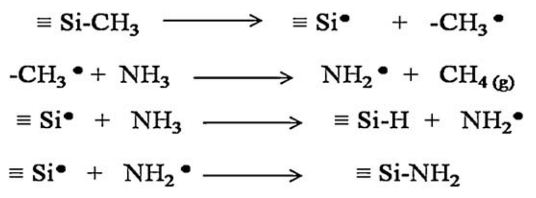
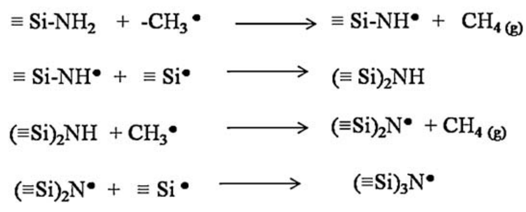


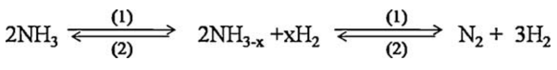
Fig. 6. Thermogravimetric curve of (a) SiCNYO powder from room temperature to 1550 °C and under isothermal conditions for 2 h at 1550 °C and (b) gaseous evolution during heat treatment under He.



Scheme 1. Reactions showing that the reduction of C may begin by the release of CH_4.



Scheme 2. Interaction between intermediate species that leads to trisilylated atoms ($\equiv$Si)$_3$N.



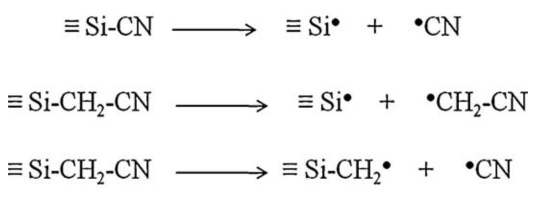
Scheme 3. Thermodynamic decomposition of NH_3.

The different reactions presented in Scheme 2 show that intermediate species ($CH_3^{\bullet}$, $NH_2^{\bullet}$, $Si^{\bullet}$, etc.) interact together, thus leading to trisilylated atoms ($\equiv$Si)$_3$N, which are stable structures at high temperature.

Above 700 °C, NH_3 should thermodynamically decompose into N_2 and H_2. However, previous studies have shown that intermediate species such as NH_{3-x} can appear during the decomposition and participate in the cleavage of Si–C bonds (Scheme 3).[17] Determining the decomposition rate of NH_3 seems difficult, considering both the thermodynamic and kinetic aspects. Nevertheless, this phenomenon is a key point in controlling the powder composition.[5]

Thermodynamically, the introduction of H_2 into the carrier gas must shift the equilibrium toward the left side and limit the decomposition of NH_3. Nitridation from molecular N_2 is not possible below 1400 °C; therefore, the increased amount of N introduced into the powders must be due to the reactivity of NH_{3-x} intermediate species.

Moreover, a part of the C evolves as hydrocarbons (C_xH_y),[8] but the C release (in the form of HCN and RC≡N) seems to be facilitated by the presence of H_2 in the pyrolysis atmosphere, as evidenced by the FTIR spectra.[18] This finding illustrates the effective role of H_2 coupled with NH_3 limiting the formation of cyano groups (CN). Scheme 4 presents the main reactions at the origin of the formation of a CN group during the decomposition of the precursor at high temperature.



Scheme 4. Principal reactions at the origin of the formation of CN group.

To verify whether the Si_3N_4–SiC composite can be formed without free C after heat treatment, the as-pyrolysed powders were annealed up to 1550 °C.

3.2. Thermal stability

The thermal stability of the as-pyrolysed SiCNYO and SiCNAl(O) powders was studied by TGA.

3.2.1. SiCNYO powders

We discuss only results for SiCNYO powders obtained with 10% H_2 in 25% NH_3. To accentuate the phenomena occurring during the thermal treatment, the experiments were carried out on powders under a dynamic gas mixture (He/N_2, 20/80 vol.%, 99.95% purity) with a flow rate of 0.08 L min^{-1}.

Fig. 6(a) presents the curve of the weight loss of SiCNYO powders by temperature and under isothermal conditions for 2 h at 1550 °C. We can distinguish 3 steps: one between room temperature and 1300 C with a low weight loss (<1%), one in the 1300–1550 °C range corresponding to an important mass loss (21%), and one at 1550 °C, when the powders are thermally stable. Indeed, with the furnace used for the synthesis, raising the furnace temperature beyond 1400 °C to try to obtain a higher stability of the as-pyrolysed powders is technically impossible.

The gaseous species formed up to 1550 °C were characterized by mass spectrometry (Fig. 6(b)) adjusted for the detection of volatile species traces.

First, under inert atmosphere (He) and between 500 and 900 °C, numerous gaseous species were detected. The main evolution corresponds to CH_4 ($m/z = 15$), which can be obtained by the recombination of the $H^{\bullet}$ and $CH_3^{\bullet}$ radicals formed by the rupture of the chemical bonds during heat treatment.

We observed cyano groups (C≡N) such as CH_3–C≡N ($m/z = 41$) and HC≡N ($m/z = 27$) at temperatures <900 °C. These species can be obtained similarly by the recombination of $H^{\bullet}$ and $^{\bullet}CH_2$–C≡N radicals.[16] The same temperature range revealed a weak gaseous species with $m/z = 44$, which could correspond to CO_2 formed by combustion of a part of C with traces of O contained in the carrier gas.

Second, the most important weight loss occurred above 1300 °C, with the formation of SiO and/or CO_2 ($m/z = 44$), CO ($m/z = 28$) and N_2 ($m/z = 28, 14$). These species appeared during the decomposition of the phase of the amorphous oxycarbonitride silicon, $SiC_xN_yO_z$, and the structural reorganization.[19] The mechanism of atomic redistribution and structural reorganization of elements within the material could take place in this temperature range.

The spectrum of the ^{29}Si NMR for the heat-treated SiCNYO powders (Fig. 7) showed a broad peak from 0 to −30 ppm and a thin split peak with an apex at −47 ppm. During post-treatment, the powders go through important structural modifications. The refinement of the peak at −47 ppm could illustrate better crystallinity of powders and organization of SiN_4 environments after annealing, whereas the broad one at −15 ppm suggests that the structural organization of the SiCN phase is incomplete. The peak deconvolution clearly showed a contribution of different environments at −11, −15 and

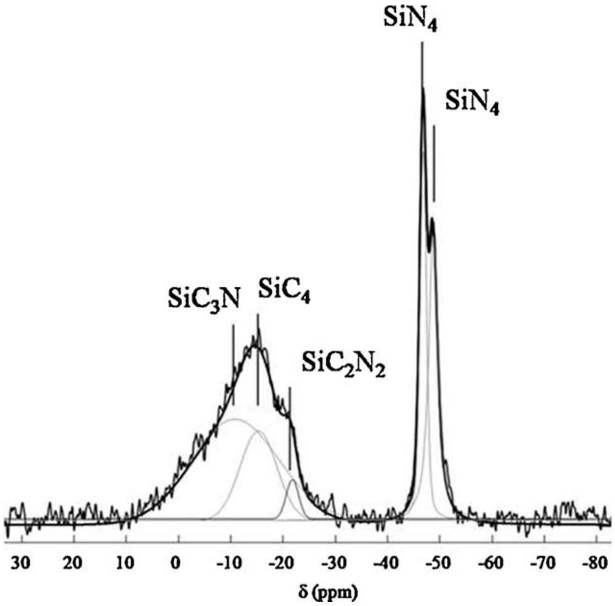


Fig. 7. ^{29}Si NMR spectrum of SiCNYO powder treated at 1550 °C for 2 h.

−22 ppm, which can be attributed to $\underline{Si}C_3N$, $\underline{Si}C_4$ and $\underline{Si}C_2N_2$, respectively.

The XRD pattern of the SiCNYO powders was registered after TGA experiments (Fig. 8). The different crystalline phases formed after the heat treatment were α-/β-Si_3N_4 and β-SiC. A smaller quantity of Y_2SiO_5 was also detected.

3.2.2. SiCNAl(O) powders

The heating conditions were chosen to compare these results to those of a previous study.[5] The as-pyrolysed powders obtained with 5% and 25% NH_3 coupled with 10% H_2 containing high and low C content, respectively, were annealed at 1550 °C for 2 h under a N_2/He (20%/80%) atmosphere. As for SiCNYO powders, the experiment was performed with cold-pressed powders embedded into the same powder to avoid a composition changing during the annealing and to keep the thermal conditions as close as possible to the sintering ones. The chemical analysis indicates (Table 6) that the C/N ratio was stable for the powder obtained with 25 wt.% NH_3, whereas this ratio increased for the powder obtained with 5 wt.%.

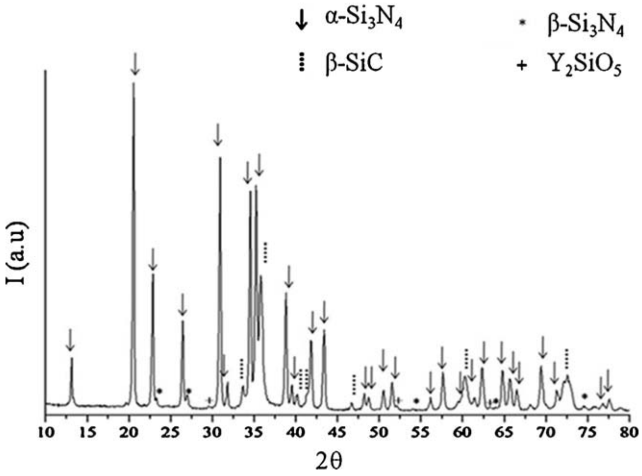


Fig. 8. X-ray diffraction (XRD) spectrum of SiCNYO powder after annealing at 1550 °C for 2 h under N_2.

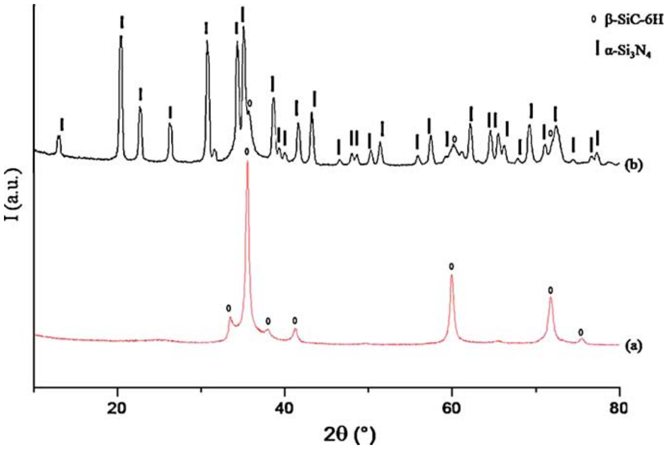


Fig. 9. XRD spectra of SiCNAl(O) powder pyrolysed with (a) 5% and (b) 25% of NH_3, heat treated for 2 h at 1550 °C under N_2/He (20%/80%).

The corresponding XRD spectra in Fig. 9 demonstrate that the C-rich powder (a) crystallizes into SiC (6), whereas the structural organization of the powders containing a suitable C/N ratio (b) leads to the formation of Si_3N_4, as well as SiC but on a lower scale.

The presence of H_2 in the pyrolysis atmosphere (Ar/NH_3/H_2) resulted in an evolution of the powder compositions. By changing the amount of NH_3, the SiC/Si_3N_4 ratio could be modulated.

To compare the transformation rate of the powder structures with temperature, the structural evolution of C was followed by Raman spectroscopy for the as-pyrolysed powders, as well as for the same batches annealed at 1550 °C and at 1750 °C for 2 h (Fig. 10).

The as-synthetized powders showed Raman bands at 1600 and 1350 cm^{-1}, which characterize free C with the E_{2g} and A_{1g} Raman modes, respectively.[20–22] The intensity was low for the (b) spectrum because of a lower C content in the as-pyrolysed powder. This finding evidences the beneficial effect of H_2 (coupled with 25% NH_3). Treatment at 1550 °C led to a similar C organization in the 2 batches, but the band intensity was lower for the (b) spectrum. Powders must be heated at 1750 °C to observe a distinct difference. This post-pyrolysis treatment involved an *in situ* crystallization of SiC characterized by the formation of new bands at about 790 cm^{-1} and 960 cm^{-1} for (b) and only one at 800 cm^{-1} for (a). This difference could be due to the kind of SiC polytypes formed in each powder.[21,22] The truncated band with the top situated from 765 to 800 cm^{-1} corresponds to a multiple band, which can be assigned to a hexagonal polytype, as well as the band at 970 cm^{-1}. The initial C content and its environment seem to influence the structural organization of the powders. After the post-treatment at 1750 °C, we can deduce that the decrease in the intensity of bands at 1600 and 1350 cm^{-1} indicates a better C atom arrangement with both NH_3 and H_2 introduced in the reactive atmosphere (Fig. 10b)).

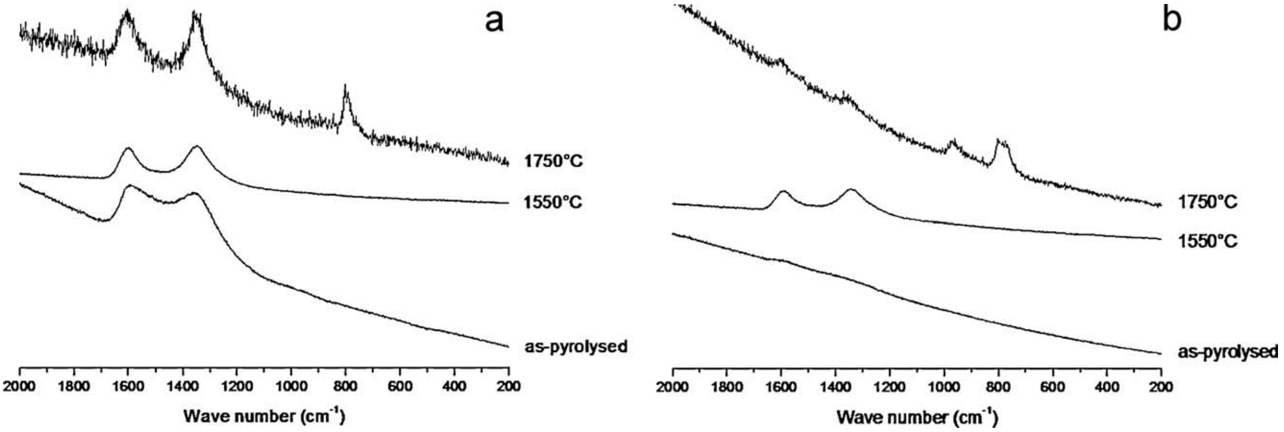


Fig. 10. Raman spectra of the as-synthesized powders and after annealing at 1550 °C and 1750 °C: synthesis under Ar/NH_3/H_2 (10% H_2) with (a) 5% NH_3 and (b) 25% NH_3.

Table 6
Comparison of the C and N contents of the as-pyrolysed (with 5% and 25 wt.% of NH_3 + 10% H_2) and the corresponding powders after annealing.

H_2 wt.%	NH_3 wt.%		Chemical composition (wt.%) and equivalent molar ratio		
			C	N	C/N
10	5	After pyrolysis	30.2	24.4	1.5
		After annealing	33.6	5.8	6.8
10	25	After pyrolysis	8.7	38.2	0.25
		After annealing	8.6	33.1	0.3

4. Conclusions

We studied the influence of the NH_3/H_2 mixture in the atmosphere during spray-pyrolysis of SiCNYOH and SiCNAlH organometallic precursors. The control of free C content is key to the production of stable Si_3N_4/SiC materials. The introduction of H_2 into an Ar/NH_3 mixture leads to a modification of the rate of NH_3 decomposition. Pyrolysis in a reactive Ar/NH_3/H_2 mixture can diminish the C content by release of gaseous species containing C (C_xH_y, HCN, RCN) and stabilizing the nitriding species (NH_{3-x}). These conditions can lead to better control of the composition. The use of a reactive atmosphere with Ar/H_2/NH_3 is also important for controlling the thermal stability of powders. We obtained Si_3N_4/SiC composites after an annealing of the powder (2 h at 1750 °C) synthesized with 25% NH_3 and 10% H_2. Heat treatment revealed that the SiCN system cannot be stabilized during pyrolysis because of the short residence time of the species inside the reactional zone and the limited pyrolysis temperature (1400 °C).

Studies of the sinterability of pre-alloyed powders containing suitable amounts of Y and O as heteroelements are in progress. Preliminary tests of powder sinterability have shown that the viscous behaviour of the material promotes densification. A new crystalline phase, containing Y, Si and O elements, is detected after cooling. Thus, experiments are in progress to introduce Y, Al and O in the same precursor. The first tests of synthesis of SiCNAlYO powders and the sintering step of these nanopowders seem promising. The presence of an increased quantity of heteroelements in the material would favor its total densification.

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