

Si/C/N nanocomposite powders with Al (and Y) additives obtained by laser spray pyrolysis of organometallic compounds

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Amorphous Si/C/N nanopowders have been synthesised by laser spray pyrolysis of hexamethyldisilazane— $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ or HMDS—using a high power tuneable continuous wave CO_2 laser and the ultrasonic injection into the laser beam of fine liquid droplets which form an aerosol. Effects of laser power density (expanded or non expanded laser beam) and addition of aluminium (and yttrium) alcoxide to liquid HMDS have been studied using chemical analysis, nitrogen adsorption–desorption, infrared spectroscopy and transmission electronic microscopy (TEM) as characterisation methods. Chemical and structural changes occur with heat treatment under nitrogen at temperatures up to 1600°C . In most cases the powders containing Al (and Y) additives remain in the nanometric range, and their crystallisation is less pronounced than powders made from HMDS without Al (and Y) addition. © 1999 Kluwer Academic Publishers

1. Introduction

An increasing interest is devoted to the preparation processes of ultrafine ceramic powders with well controlled characteristics in order to enhance densification and improve properties in the final materials [1, 2].

Laser synthesis using high power continuous wave (c.w.) CO_2 laser appears to be a promising technique for the preparation of nanoscale powders with ideal characteristics for use in ceramic technology. SiC, Si_3N_4 , Si/C/N powders have been obtained using either gaseous precursors such as silane [3–6] or recently liquid organosilicon compounds [7, 8]. SiCN powders issued from mixtures of gaseous precursors (SiH_4 , CH_3NH_2 or C_2H_2 , NH_3) have been used for the fabrication of dense materials with improved mechanical properties [9] or presenting high temperature ductility [10]. In the case of synthesis from liquid precursors, hexamethyldisilazane ($(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ or HMDS) was ultrasonically pulverised to form an aerosol which is injected into the beam of a high power c.w. CO_2 laser in order to obtain Si/C/N particles. Addition of ammonia in the aerosol provides change in chemical composition [11, 12]. In these silicon carbonitride systems, silicon, carbon and nitrogen are uniformly mixed. Wakai *et al.* [13] have reported the sinterability of SiCN nanopowders obtained from the pyrolysis of HMDS vapour. Thus, dense SiC– Si_3N_4 composite materials with superplastic behaviour have been obtained by hot pressing in the presence of Al_2O_3 and Y_2O_3 as sintering aids.

In most cases, SiCN nanopowders are sintered with sintering aids such as Al_2O_3 and Y_2O_3 which form a liquid phase (YSiAlON) during heat treatment. In order to avoid the mixing process of powders (SiCN, Al_2O_3 and Y_2O_3), it is interesting to synthesise SiCN powders containing *in situ* uniformly dispersed sintering aids, i.e. alumina and yttria. This paper reports both the synthesis of SiCNAlYO nanopowders by laser spray pyrolysis of HMDS solutions containing aluminium (and yttrium) alcoxides and the characterisation of such powders. The characteristics of these powders are compared with those of powders synthesised without Al (and Y) additives.

2. Experimental

The experimental device used for the different experiments reported here has been previously described [8, 11, 12]. Briefly the liquid precursor, HMDS, neat or mixed with aluminium (and yttrium) alcoxides, is ultrasonically pulverised and injected through a glass tubing (diameter = 13 mm) into the beam of a commercial PRC—Oerlikon 1500 W, fast-axial-flow tuneable CO_2 laser which can emit between 9 and 11 μm and tuned to 10.6 μm (10P20 line) in resonance with a strong IR absorption band of HMDS [14, 15]. Argon is used as carrier gas of the pulverised solutions. Reactions occur with flame and formation of powders which are collected in a glass chamber equipped with a metallic cylindrical porous filter. The laser beam

TABLE I Composition of precursor solutions (in wt %)

Experiment	HMDS	(iPrO) ₃ Al	(secBuO) ₃ Al	(iPrO) ₃ Y	tPrOH	[Al(+Y)]/Si
	C ₆ H ₁₉ NSi ₂	C ₉ H ₂₁ O ₃ Al	C ₁₂ H ₂₁ O ₃ Al	C ₉ H ₂₁ O ₃ Y	C ₃ H ₇ OH	(atomic ratio)
HMDS 36 ^a	100	—	—	—	—	0
HSA1 00 ^a	83	—	17	—	—	0.07
HMDS 66 ^b	100	—	—	—	—	0
HSA1 03 ^b	85	15	—	—	—	0.07
HSA1 04 ^b	82	14	—	—	4	0.07
HSA1Y 05 ^b	84	9	—	3	4	0.05

^aExpanded laser beam (diameter: 26 mm); solution heating (90–100 °C).

^bUnfocused laser beam (diameter: 13 mm); solution at room temperature.

(diameter = 13 mm) can be expanded ($\times 2$) and the solution can be heated (90–100 °C) in order to increase the quantity of the displaced liquid during pulverisation. Liquid sec-butoxide and solid isopropoxide are used as aluminium precursors, solid isopropoxide is used as yttrium precursor. In two experiments (HSA104 and HSA1Y05) isopropanol has been added in order to decrease the viscosity of the solutions. Note that hexamethyldisilazane reacts sluggishly with alcohols [16, 17] and the solutions must be used as freshly prepared. Table I gives the composition of the different starting solutions (in wt % of precursor used). The [Al(+Y)]/Si atomic ratio is also reported because this parameter allows to compare the Al and Y content in precursor solutions and in as-formed powders.

As-formed Si/C/N powders (about 2 g) are slightly pressed in a teflon mould to form pellets (diameter = 20 mm; height ~10 mm) which are placed in graphite crucibles. Then they are annealed in a high temperature graphite furnace at different temperatures up to 1600 °C under nitrogen with a heating rate of 10 °C/min and a dwell time of 1 h. A comparison between a dwell time of 1 and 4 h at 1600 °C has been also established.

The changes in powder characteristics as a function of temperature treatment compared with as formed powders are followed by chemical analysis, infrared spectroscopy, transmission electronic microscopy (TEM), X-ray diffraction (XRD) and the specific surface area is measured by the Brunauer-Emmett-Teller (BET) method.

3. Results and discussion

3.1. The as-formed powders

Synthesis conditions and chemical analysis are summarised in Table II. Because of the amorphous structure of as-formed powders (see below), and in order

to compare the composition of powders and precursor solutions, the elemental composition is calculated in atoms.

The high production rate obtained in HMDS36 and HSA100 experiments compared to the other runs can be explained by the higher argon flow rate and also by the heating of the solutions which are ultrasonically pulverised, favouring formation of more dense aerosols by the decrease of viscosity [8, 11, 12]. But heating has a disadvantageous effect, inducing a preferential pulverisation of the more volatile compound of solution i.e., HMDS, as shown by the change in Al/Si atomic ratio value (0.02 in HSA100 powder compared to 0.07 in the starting solution). This value (Al/Si = 0.07) has been chosen to correspond to a 6 wt % Al₂O₃ content in a final SiC-Si₃N₄ material according to the different oxide contents reported by the literature (from about 10 [18] to, more recently, 1 wt % [19], alumina and yttria). The effect of preferential pulverisation is less pronounced when solutions are not pre-heated: [Al(+Y)]/Si atomic ratio is in the range 0.04–0.06 for HSA103, 04 and HSA1Y05 powders compared to the corresponding range 0.05–0.07 in the starting solutions.

The laser spray pyrolysis, with argon as carrier gas, gives rise to C-rich powders, as it is indicated by the high C/N atomic ratio (~3.0, Table II).

The N/Si atomic ratio of the as-formed powders is relatively stable, between 0.49 and 0.59 and very near to the corresponding value for HMDS i.e., 0.50.

The C/Si atomic ratio is lower for powders obtained with lower laser power density (expanded laser beam) i.e., 1.43 in HMDS36 sample compared to 1.46 in HMDS66 sample (see Table II). This phenomenon is linked to methyl groups issued from HMDS dissociation which form light hydrocarbons [20], less pyrolysed in the reaction zone and producing less carbonaceous

TABLE II Synthesis conditions and chemical analysis of powders

Run	Argon flow rate (cm ³ /min)	Production rate (g/h)	Elemental composition (atom number)							S _{BET} (m ² /g)
			Si	C	N	O	Al	Y	C/N	
HMDS36 ^a	2500	64	1	1.43	0.51	0.37	—	—	2.8	82
HSA1 00 ^a	2400	67	1	1.45	0.52	0.23	0.02	—	2.8	110
HMDS66 ^b	1900	31	1	1.46	0.59	0.06	—	—	2.5	66
HSA1 03 ^b	1900	34	1	1.70	0.55	0.22	0.06	—	3.1	66
HSA1 04 ^b	1900	32	1	1.81	0.49	0.53	0.06	—	3.7	81
HSA1Y05 ^b	1900	30	1	1.78	0.51	0.46	0.04	0.01	3.5	79

^aExpanded laser beam (diameter: 26 mm); solution heating (90–100 °C).

^bUnfocused laser beam (diameter: 13 mm); solution at room temperature.

compounds at relatively lower temperature when the laser power density decreases. Moreover, the addition in HMDS solution of aluminium and yttrium precursors containing carbon induces an increase of C/Si atomic ratio in powders. For HSAI(Y) samples, the C/Si atomic ratio is more important when the synthesis is carried out using high laser power density, compared with those obtained from low laser power density. High C content produces a color change in powders from beige to dark grey.

For powders without Y and Al addition, O atomic content depends on sample storage. In the case of HMDS 36 exposed to air for a long time, O content reaches 0.37 while it decreases to 0.06 in HMDS66 stored in an inert atmosphere. Alcoxide addition involves an increase in the O atomic content (about 0.23 for HSAI 00 and HSAI 03 samples). This effect is more pronounced when isopropanol is added (0.53 for HSAI 04 and 0.46 for HSAIY 05 samples). Hydrogen is not taken into account in elemental analysis, but IR spectra show the presence of Si-CH₃, N-H, C-H and O-H bonds (see paragraph no. 3.2).

All as-formed powders exhibit high specific surface area values (Table II) as previously obtained [8]. They are in the nanometric range (20–30 nm) and amorphous as has been shown by TEM and X-ray diffraction analysis.

3.2. The annealed powders

Table III shows the changes in chemical composition during heating for 1 h at 1600 °C under nitrogen atmosphere.

The chemical composition is calculated in stoichiometric compounds (Si₃N₄, SiC, SiO₂, Y₂O₃, Al₂O₃) from elemental analysis results assuming that all Al and Y are in the form of Al₂O₃ and Y₂O₃, the remaining O being in the form of SiO₂, then all N form Si₃N₄ and the remaining Si is under the form of SiC. Free carbon is the difference between total carbon and carbon bonded to Si in SiC. Such a calculation is necessary to evaluate the composition of future sintered materials, but it is approximate both for as-formed and annealed powders. Effectively, in the case of amorphous as-formed powders no crystalline compounds such as Si₃N₄, SiC, Y₂O₃, Al₂O₃ can exist. In annealed powders, Si₃N₄

and SiC exist, but Al and Y are not only bonded to O (Y₂O₃, Al₂O₃) but also may be combined in SiAlON or YSiAlON amorphous phases, as for classical sintering of silicon nitride compounds in the presence of sintering aids (Y₂O₃, Al₂O₃) [21, 22]. Note that the calculated Si₃N₄ and SiC contents should be very similar to that which exists in materials because of the low quantity of Y and Al bonded to nitrogen. First experiments of ²⁷Al MAS-NMR (Magic Angle Spinning-Nuclear Magnetic Resonance) allowed detection of N-substituted oxides on as-formed and annealed Si/C/N powders. These results, showing the change of the Al atom environment between 1400 and 1600 °C, give evidence of the formation of mixed AlO_xN_{4-x} tetrahedra [23]. Note that such a structure is not the SiAlON predicted compound and could be explained by carbonitridation of Al-O bonds.

The changes in composition (Table III) to SiC rich compounds, during annealing at 1600 °C, are linked to the decomposition of nitrogenous species (SiCN, Si₃N₄) occurring from 1450 °C. Such decomposition is important because of the high carbon content in as-formed powders (C/N > 0.75) [11, 12]. Effectively, EXAFS analysis of C rich powders synthesised from HMDS [24] have shown that the atomic local arrangement of Si is essentially composed of mixed SiC₃N tetrahedra and of SiC₄ tetrahedra which are already close to the SiC structure. This suggests the decomposition of slightly nitrogenous compounds (SiC₃N) during annealing in order to reach the SiC structure. Moreover, annealing induces a decrease in silica and in free carbon content because of the carbonitridation of this compound which involves CO evolution.

After a one hour annealing treatment at 1600 °C, the C/N atomic ratio is around 15 for HMDS powders while it is only of 4.3 to 5.1 for HSAI(Y) powders (Fig. 1), indicating that the loss of nitrogen decreases for powders containing Al and Y additives. This suggests that the decomposition of N containing species (SiCN, Si₃N₄) is limited during heat treatment of HMDS powders with Al (and Y) additives, probably due to the formation of a liquid phase in the quinary Y-Si-Al-O-N diagram preventing the degradation of nitrogenous compounds.

Moreover, for powders without additives the SiC content is high after annealing (up to 83–90 wt % in HMDS

TABLE III Changes in chemical composition after annealing at 1600 °C

Powder sample	Annealing temperature (°C)	Chemical composition (wt%)					
		Y ₂ O ₃	Al ₂ O ₃	SiO ₂	Si ₃ N ₄	SiC	Free C
HMDS 36	25	—	—	18.2	29.3	28.1	19.6
	1600	—	—	2.2	5.5	89.8	0.7
HSAI 00 (AlsecBuO)	25	—	2.1	10.2	31.3	35.6	19.5
	1600	—	3.0	0	17.3	75.3	4.8
HMDS 66	25	—	—	3.4	38.3	39.0	19.3
	1600	—	—	1.5	6.2	83.0	9.9
HSAI 03 (Al <i>i</i> PrO)	25	—	4.7	6.5	32.3	34.3	22.1
	1600	—	2.8	0	17.8	70.2	10.4
HSAI 04 (Al <i>i</i> PrO + <i>i</i> PrOH)	25	—	4.5	20.8	26.8	25.2	22.6
	1600	—	7.1	0	18.3	66.7	8.1
HSAIY 05 (AlY <i>i</i> PrO + <i>i</i> PrOH)	25	1.7	3.2	18.1	28.0	26.3	22.7
	1600	1.3	3.8	0	19.3	64.1	9.0

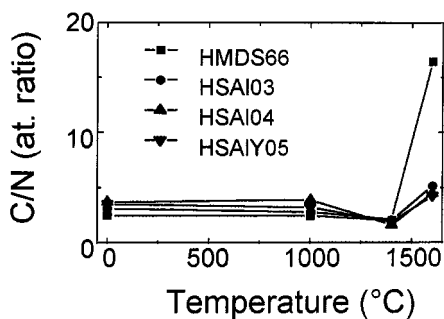
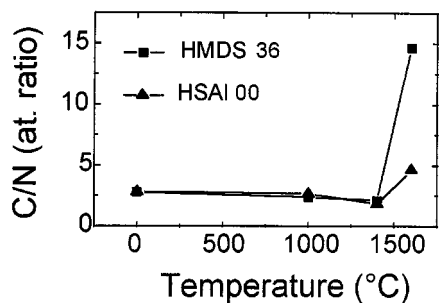


Figure 1 Evolution of the C/N atomic ratio with annealing temperature.

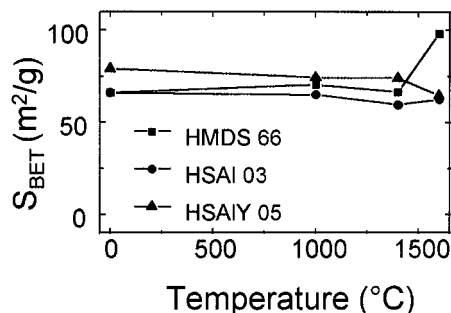
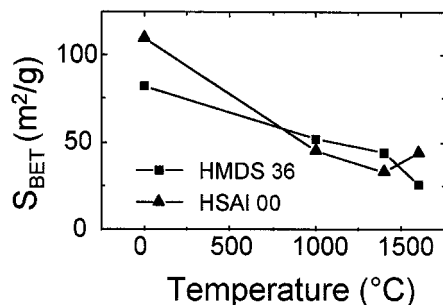


Figure 3 Evolution of the specific surface area (S_{BET}) with annealing temperature.

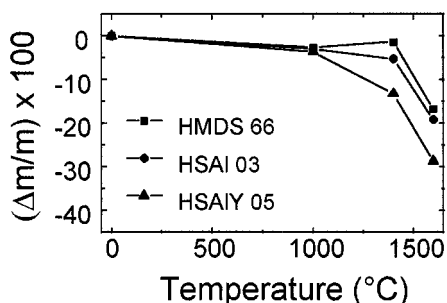
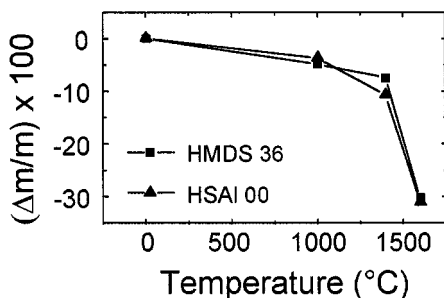


Figure 2 Weight losses obtained during annealing under nitrogen.

36 and 66 samples), in comparison with powders containing Al (and Y) additives for which the SiC content is lower (64–75 wt %) and the Si_3N_4 is higher. This result confirms the slower decomposition of nitrogenous species in Al (and Y) additives containing powders.

Weight changes are plotted as a function of annealing temperature on Fig. 2. Weight losses are observed and confirm the decomposition of powders. They increase with temperature and they reach 17–30% range at 1600 °C for 1 h. Higher values are observed for powders with high O content (HSAIY 05) which induces a more important carbonitridation of the silica with CO evolution as shown previously by thermogravimetric analysis coupled with mass spectrometry [8, 11, 12].

When the dwell time at 1600 °C increases from 1 to 4 h, a slight change in weight loss is observed (difference of 2%).

Changes in the specific surface area, S_{BET} , with annealing temperature depend on the synthesis conditions and essentially on the C and O contents (Fig. 3). For powder without additives, the S_{BET} value of HMDS 36 sample (high O content) obtained with low laser power density decreases continuously when annealing temperature increases (25 m^2/g for annealed powder at 1600 °C for 1 h, Table III) and the remaining C content is low indicating that the total free carbon has been consumed by the carboreduction of the silica. On the contrary, in HMDS 66 sample with low initial O content, the silica consumes partially the free carbon and after annealing at 1600 °C there remains sufficient carbon (about 10 wt %) to create fine particles leading to an increase in the S_{BET} value. For powders containing additives and obtained with high laser power density (HSAI 03, 04 and HSAIY 05 samples) no significative change in S_{BET} value is observed because of the high remaining free carbon content (8–10 wt %) after heat treatment. In HSAI00 sample, heat treatment leads to a decrease in specific surface area with temperature because of the low remaining free C content after treatment (4.8 compared to 8–10 wt % in other samples). After annealing at 1600 °C during 4 h, a slight decrease in specific surface area is observed for HMDS66 and HSAI00, 03 and 04 powders while for HSAIY05 sample containing yttrium the decrease in S_{BET} is more important (–35 m^2/g) suggesting grain growth.

Changes in the infrared spectra are observed during annealing (Figs 4 and 5). The as-formed powders present broad bands centred near 1000 cm^{-1} and including Si–C and Si–N bonds together (which suggests amorphous SiCN compounds) with some remaining hydrogenated compounds like Si– CH_3 at 1250 cm^{-1} .

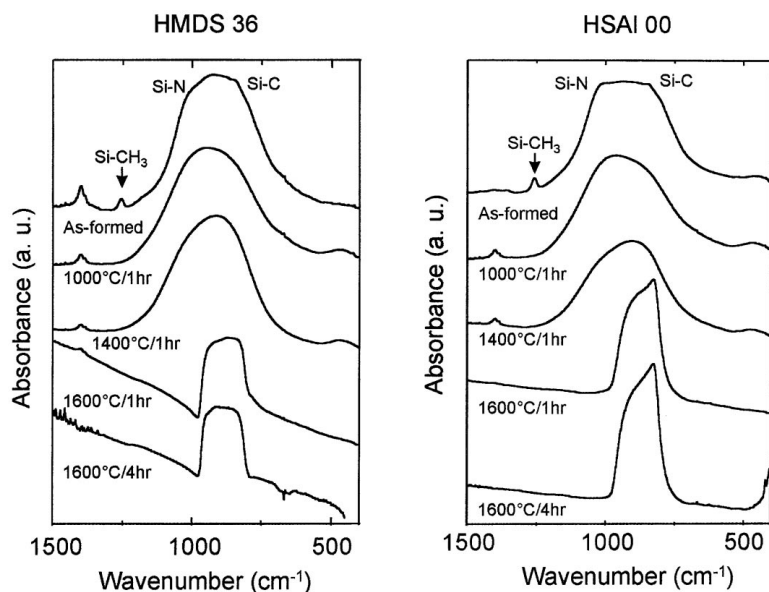


Figure 4 Change in IR spectra for samples HMDS36 (without additive) and HSAI00 (with Al additive) during annealing.

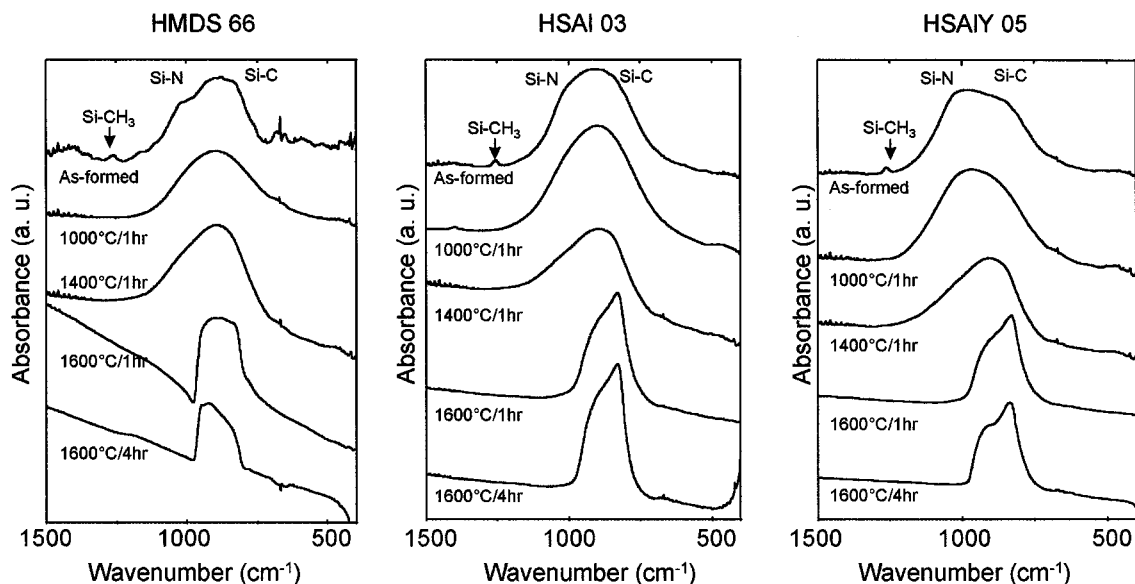


Figure 5 Change in IR spectra for samples HMDS 66 (without additive), HSAI 03 (with Al additive) and HSAIY 05 (with Al and Y additives) during annealing.

At 1000 °C the spectra are always broad with a weak band below 500 cm^{-1} corresponding to the Si–N bond. At 1400 °C the main absorption band is displaced toward lower wavenumbers corresponding to the Si–C bond. At 1600 °C the absorption band of SiC remains with a maximum at 870 cm^{-1} . But in the meantime a difference is observed for the powders containing Al (+Y) additives which have a flat base line in their IR spectrum (Fig. 4) whereas a pronounced dip appears near 1000 cm^{-1} in the IR spectrum of powders without additives (Fig. 5) indicating crystallisation or grain growth as observed previously in annealing of SiC powders obtained by a laser gas-phase driven reaction [25] or from pyrolysis of a polycarbosilane [26]. No significant change is observed when the dwell time increases from 1 to 4 h. TEM observations and XRD patterns obtained from HMDS and HSAI(Y) samples annealed at 1600 °C confirm the above results.

XRD patterns are shown in Fig. 6. Powders with additives (HSAIY 05 and HSAI00 samples) present broad diffraction lines which are indicative of poor crystallisation (Fig. 6a and c). The XRD diagrams are characterised by the main peaks (111), (220) and (311) assigned to the cubic β -SiC at $2\theta = 35.6, 60.0$ and 71.8° respectively for the $\text{CuK}\alpha$ radiation. There is also evidence for the presence of 2H-SiC phase (an α -SiC polytype) with lines at $2\theta = 33.6, 38.1$ and 65.2° for the three main peaks. Changes after increasing annealing time (Fig. 6b and d) are less pronounced for the sample HSAI 00 than for the sample HSAIY05 containing both Al and Y which presents well-crystallised 2H-SiC and β -SiC as shown by the well defined peak at $2\theta = 49.8^\circ$ (Fig. 6b). For powders without additives (HMDS 36 sample only presented in Fig. 6e and HMDS 66 sample has a similar X-ray diffractogram), the diffractogram obtained for an annealing duration of 4 h presents the

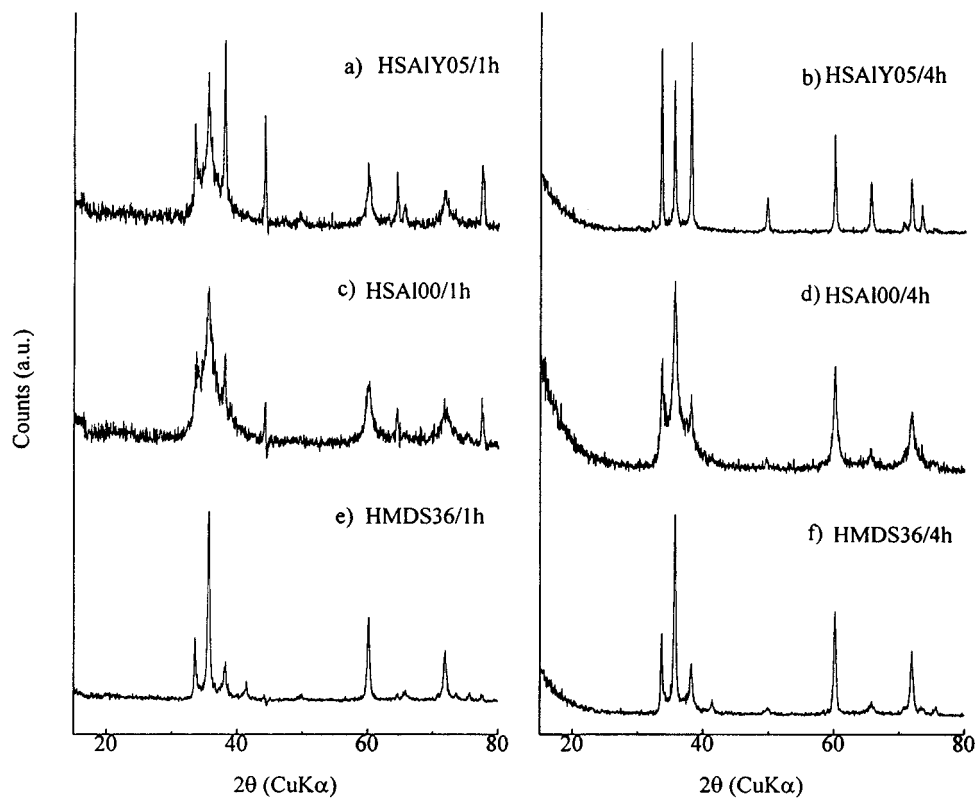


Figure 6 XRD patterns of samples HSAIY05 (with Al and Y additives), HSAI00 (with Al additive) and HMDS36 (without additive) after 1 and 4 h annealing under nitrogen at 1600 °C.

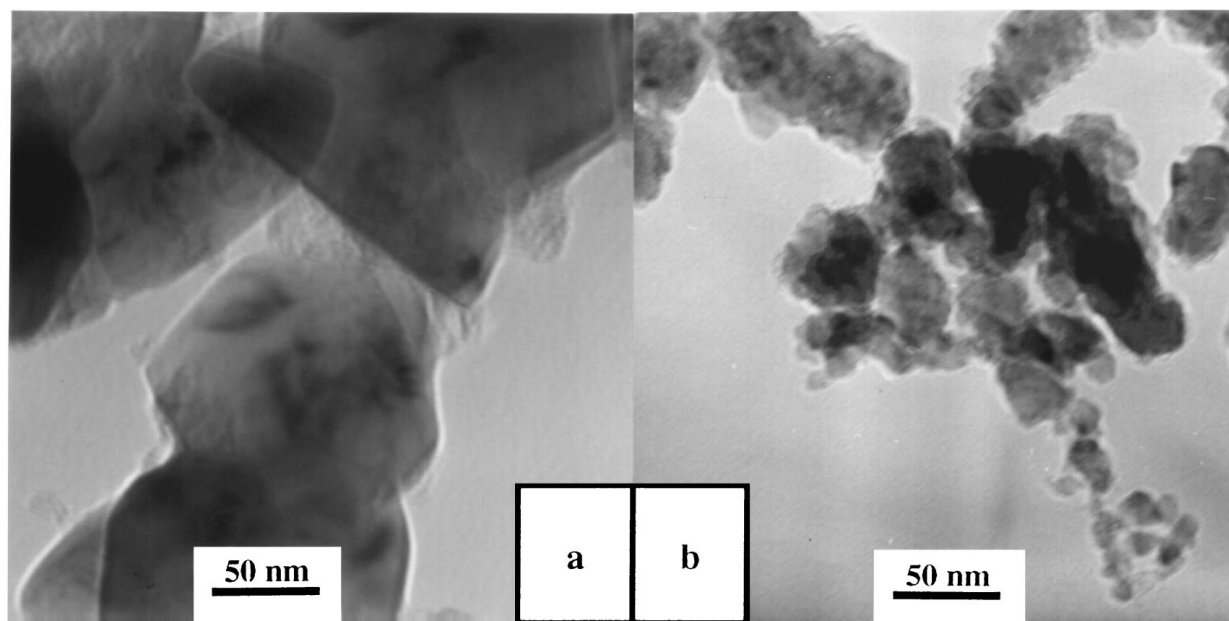


Figure 7 TEM micrographs of samples HMDS36 (a) and HSAI00 (b) after annealing at 1600 °C (1 h).

same features (Fig. 6f). One can estimate the apparent crystallite size at $2\theta = 60.0$ and 71.8° (according to the Scherrer's equation) i.e., ~ 20 , 8 and 12 nm for HMDS 36, HSAI00 and HSAIY 05 samples respectively. These values are from one-third to one-fifth of the sizes calculated from BET measurements. Similar differences have been obtained in the case of well-crystallised silicon particles obtained by laser pyrolysis of silane [3]. Very close results are obtained for HSAI 03 and 04 samples.

TEM micrographs of samples obtained with low laser power density and annealed for 1 h at 1600 °C are shown in Fig. 7. Fig. 7a presents well-formed crystallites in the 100–200 nm range for HMDS 36 sample. On the contrary, HSAI00 sample (Fig. 7b) shows the presence of particles with lower dimensions (30–70 nm) containing very small inclusions. In further characterisations, TEM observations coupled with EDS analysis would be needed for the identification of these inclusions. Annealed samples (1 h, 1600 °C), from powders obtained

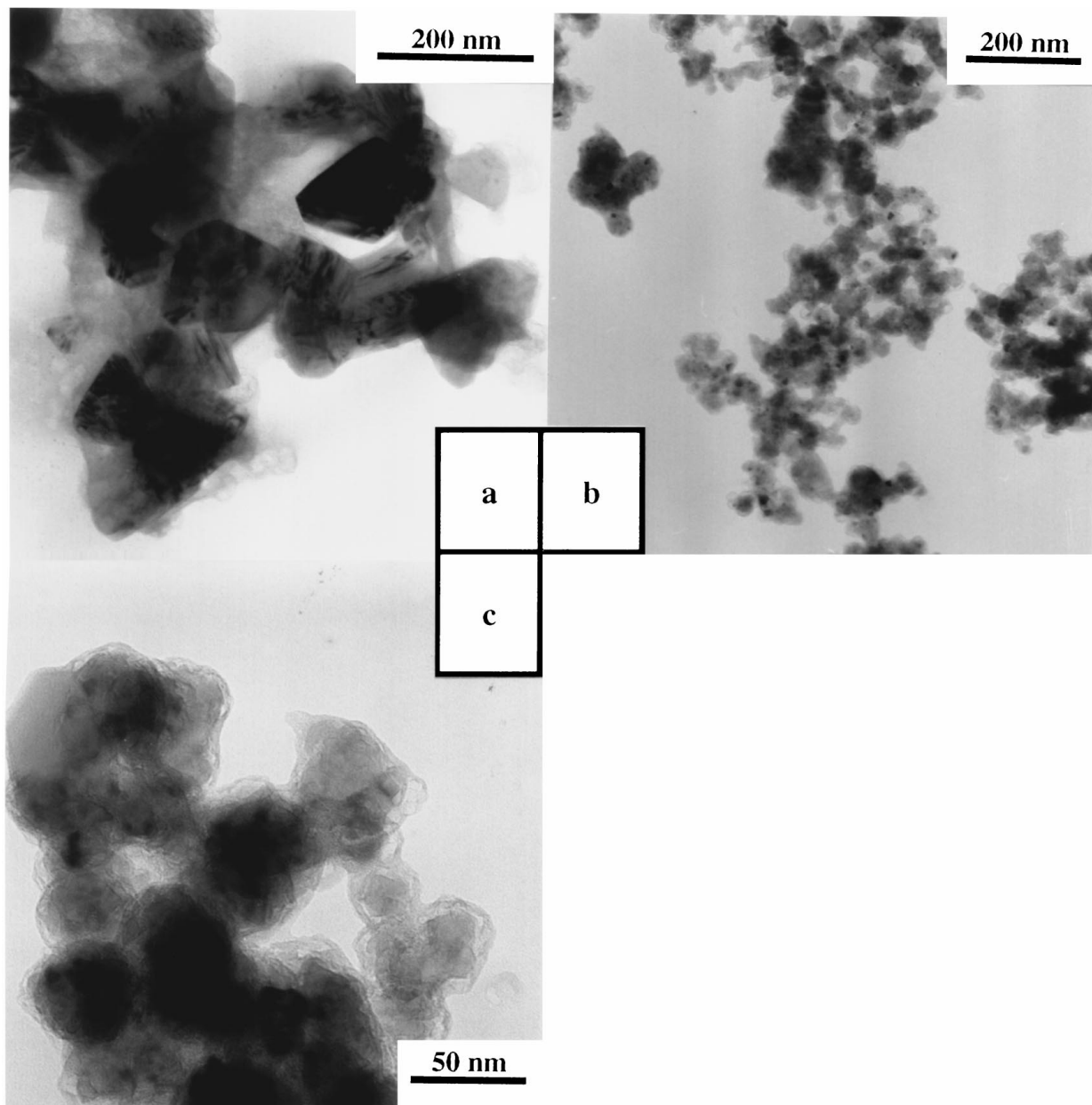


Figure 8 TEM micrographs of samples HMDS66 (a), HSAIY05 (b) and HSAI03 (c) after annealing at 1600 °C (1 h).

with high laser power density and containing more free carbon, present similar TEM images (Fig. 8). HMDS 66 sample (Fig. 8a) is composed of crystallites in the 100–150 nm range. The particles obtained from powders with additives are smaller—below 50 nm—as shown in Fig. 8b for HSAIY 05 sample. In a magnification image (Fig. 8c of HSAI 03 sample) the particles appear to be embedded by thin layers formed presumably of ribbon carbon from fine particles which have migrated to the surface during the heat treatment.

4. Conclusion

This work shows that it is possible to introduce, during the synthesis by laser spray pyrolysis, elements of sintering aids (Al, Y and O) into the SiCN chemical system. The pyrolysis with argon as carrier gas, allows to obtain amorphous C-rich nanopowders (C/N ~ 3.0).

Among the different synthesis parameters, the heating of the precursor solution induces a decrease in Al and Y content in as-formed powders, compared

with non-heated precursor solution. Moreover, when the laser power density is high and/or when Al (and Y) precursors are added to HMDS solution, the C content in as-formed powder increases.

Thermal treatment up to 1600 °C of as-formed powders induces weight losses as well as chemical and structural changes. In particular, whatever the powder (with or without Al (and Y)), decomposition of nitrogenous species and crystallisation of SiC-rich system occur during annealing. *In situ* sintering aids elements limit the decomposition of nitrogenous species. Moreover the crystallisation degree of powders with *in situ* Al (and Y) is less pronounced than powders without Al and Y. This phenomenon suggests the formation of a liquid phase during annealing, involving a solution precipitation process which limits the decomposition. Concerning the grain size, heat treatment involves grain growth which is limited when powders contain *in situ* Al (and Y).

Future studies will be concerned with the dual effects of addition of reactive gases (like ammonia) to

the carrier gas and addition of variable quantities and ratios of aluminium and yttrium alcoxides to HMDS on the structure and chemical composition of powders. Moreover, the local atomic arrangement will be studied by methods like MAS-NMR, XPS and EXAFS, and the sinterability of such powders will be tested by hot-pressing.

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Received 6 August 1998
and accepted 21 April 1999