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Nanosized Si/C/N composite powders formed by laser-aerosol coupling

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ABSTRACT

Recently it has been shown that ultrafine preceramic Si/C/N powders in the nanometric range can be obtained by combining the ultrasonic injection of a liquid precursor with the CO₂ laser irradiation. At the CEA the first experiments were conducted with hexamethyldisilazane - (CH₃)₃SiNHSi(CH₃)₃ - (or HMDS) as the precursor. The aerosol droplets formed by the Pyrosol process are carried out with a flow of argon or argon - ammonia mixture into the beam of a high powered industrial continuous wave CO₂ laser. At laboratory scale up to 100cm³/hr of liquid are displaced with a conversion efficiency (liquid → powder) of about 45%. The chemical composition is controlled by varying the synthesis conditions. The C/N atomic ratio changes from 3 (under argon) to 0.35 (under argon + ammonia). The as-formed powders are amorphous, monodispersed and nanosized (<100nm). The effect of heating under nitrogen atmosphere has been studied by various diagnostics (chemical analysis, BET, XRD).

1. INTRODUCTION.

Materials with novel properties are obtained when the constituent phase morphology is reduced to nanometer dimensions (1). A significant improvement in thermomechanical properties can be achieved by the use of homogeneous nanophase powders for various compositional systems (for example, Si/C/N). The growing interest in Si/C/N nanocomposite ceramics is also explained by their large range of properties from superplastic to a high strength and toughness, depending on the composition (2). The performances of the final products are strongly affected by the properties of the original powders, therefore the synthesis of such powders must be carefully controlled. In this respect, the laser - induced synthesis appears as ideal. The reactions are conducted in a confined, well defined wall-less zone having rapid and cooling rates and occurring with fast reaction time which can be controlled by varying the flow rates of the reactant gases or the reactor pressure. Silane has been the most extensively used precursor

in laser production of Si - based ceramic powders. But it remains too expensive and hazardous to scale up the process and recently, nitrogeneous organosilicon compounds are preferred (3).

This paper reports the synthesis of Si/C/N powders using hexamethyldisilazane (HMDS) injected in the aerosol form into the beam of a high powered CO₂ laser which is strongly absorbed by the aerosol.

2. EXPERIMENTAL.

The experimental device is shown on the Figure 1 and has been described elsewhere (4). The aerosol droplets are generated by a piezoelectric transducer placed in a glass jar (Pyrosol 7901 model from RBI) and carried out into the expanded beam (X2) of a high powered CO₂ industrial laser (CILAS CI1000). The powders are collected in a glass chamber equipped with a cylindrical metallic filter heated at about 120°C. Heating treatments under flowing nitrogen are performed at atmospheric pressure in a high temperature graphite furnace (model GE80 from Pyrox) at various temperatures between 1000 and 1600°C. Different methods are used to characterize the as-formed and the annealed powders : chemical analysis, IR spectroscopy, X-ray diffraction, BET method and TEM.

3. RESULTS AND DISCUSSION.

3.1. Laser synthesis.

Table I presents the main parameters of the synthesis for a laser power of 600W and the production results with the chemical analysis and the determination of the specific surface area (S_{BET}).

Run	Carrier gas flow rates (cm ³ /min)		Duration (min)	Production yield (g/hr)	Conversion rate (%)	Chemical analysis (wt%)			C/N atomic ratio	S _{BET} (m ² /g)
	Argon	NH ₃				C	N	O		
03 ^a	2000	0	54	20.8	n.m.	29.9	11.6	6.8	3.0	133
06 ^a	1200	620	32	14.8	n.m.	6.7	22.5	18.0	0.35	136
22 ^a	1900	0	28	22	34	28	13	9.0	2.2	139
28 ^b	2640	0	59	38	46	30	12	6.0	2.5	88
29 ^b	2660	275	63	30	39	24	17	8.0	1.4	167
31 ^b	2080	725	74	28	44	19	23	6.0	0.8	116
32 ^b	2660	140	75	28	44	25	18	7.0	1.4	95

^a : inlet diameter = 9mm; ^b : inlet diameter = 13mm; n.m. = not measured.

TABLE I. Synthesis conditions and chemical analysis results.

Up to 100cm³/hr of liquid have been displaced (Run28) with a conversion efficiency (liquid → powder) of 46%. The current experiment is stable for more than one hour and sufficient powder quantities have been collected to perform characterizations on the as-formed powders and to follow the evolution of the structure after annealing experiments.

From chemical analysis it appears that the (Si+H) content remains about constant near 50%. The N-rich powders are more sensitive to the oxidation and the O content can be high, the powders being handled in air without any special care.

The color of the powders varies from black or grey for a C-rich powder which contains an excess of free carbon to yellow or ivory for a N-rich powder, identical to a Si₃N₄ powder prepared by laser pyrolysis of a SiH₄ - NH₃ mixture.

The as-formed powders are amorphous through X-ray diffraction analysis. TEM observations reveal a monodispersion in the particle size centered below 100nm as shown on the Figure 2. The TEM results are confirmed by the high specific surface areas (generally >100m²/g) obtained by the BET method.

IR spectroscopy on the as-prepared powders has been previously reported (4) and shows the presence of N-H, Si-H, C-H and Si-CH₃ bonds with a broad band between 1100 and 800cm⁻¹ which is usually

attributed to Si-C, Si-O and Si-N bonds. The N-rich powders present a band in the 460cm^{-1} region attributed to the Si-N bond.

3.2. Annealing treatments.

Up to 1000°C the weight loss between 2 and 8% is essentially due to the evolution of hydrogenated compounds : CH_4 , H_2O or NH_3 (4). Figure 3 shows the evolution under a nitrogen atmosphere of the weight per chemical element (Si,C,N and O) as a function of the annealing temperature, supposing an initial weight of 1000mg. These measurements are consistent with the observations obtained by other methods and reported elsewhere (4,5). Between 1000 and 1400°C the weight of nitrogen increases indicating an activity of N atoms on the powder. Then the nitrated phases become unstable and decompose with evolution of N_2 as shown on the TG-MS analysis curves (4). At higher temperature the powder which has remained amorphous up to 1400°C is very well crystallized as shown on the Figure 4 for the powder HMDS03. On the XRD pattern the cubic β -SiC phase and the 2H-SiC phase (an α -SiC polytype) are unambiguously identified.

An identical annealing treatment for a N-rich powder (HMDS06) leads only to the formation of α - Si_3N_4 as shown also on the Figure 4.

Other recent results on the characterizations of the annealed powders have been reported (4,5) and an interesting zone appears in the $1400 - 1500^\circ\text{C}$ region where occurs the amorphous $\rightarrow$ crystalline morphology change. Elaborated characterization methods such as MAS-NMR of ^{29}Si , XPS, EXAFS or neutron diffusion will be needed with the aim to identify the amorphous phases.

4. CONCLUSION.

It has been shown that the coupling between an aerosol of a Si/C/N liquid precursor and the CO_2 laser irradiation is a new route to obtain nanocomposite ceramic powders. Further studies will be concerned by sintering experiments which will need powders in relative high amounts. It is necessary to increase the production and the yield of the synthesis reactions and to find other low cost liquid precursors with higher Si-content but more viscous to scale up the process.

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FIGURE 1. Schematic of the laser - aerosol coupling.

FIGURE 2. Microphotograph of an as - formed powder (bar = 100nm).

FIGURE 3. Evolution of the chemical composition during annealing.

FIGURE 4. XRD patterns of annealed powders : C-rich (top); N-rich (bottom).