I SYNTHESIS REPORT

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TITLE : **LASER NANOSCALE POWDERS**

PROJECT
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II. COST EFFECTIVE LASER SYNTHESIZED NANOSCALE POWDERS.
CASES OF THERMOMECHANICAL APPLICATIONS.

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Ill. ABSTRACT

The project is devoted to the development of laser synthesized nanoscale powders using low cost liquid precursors. Silazane and polysilazanes from ATOCHEM have been experienced. The nebulisated liquid precursor is brought into the laser beam by a carrier gaz. Such precursors strongly absorb the radiation of C02 laser: 10,6 micron. The hexamethyldisilazane has been used for the production of (Si,C,N) amorphous nanopowders. The production rate was 50 g/h and the silicium yield 60 o/o. The powder has been processed into granules via spray drying. Heat treatment up to 1600°C makes the amorphous powder to crystallize into SiC and Si3N4, with adjustable proportion. A diffraction grid has been adapted on a C02 OERLIKON laser by RADIUS ENGINEERING in order to make it tunable. New precursors have been experienced, such as hexamethyldisiloxane which gave amorphous powders of (Si,C,O). Nanopowders of tungsten carbide WC have been prepared from WF6 and C2H2 as precursors with SF6 as photosensibilisator. Heat treatments of the powder have been performed by CERAMETAL. Little amounts of remaining sulfur appeared to be detrimental for cutting tool applications. Insertion of SiC powder into erosion resistant coatings was achieved with a good dispersion of the SiC nanopowder within a nickel or cobalt matrix. Heat treatments, processing of SiC and (Si,C,N) powders were fullfilled by VITO. A study of sintering conditions resulted in preparation of dense samples, with fine microstructure.

IV. INTRODUCTION

A growing interest is devoted to production and development of composite ceramics with improved thermomechanical properties, with recent interest in reducing dimensions of constituting phases down to 100 nrn or less. Examples of such attractive materials are the structural ceramic nanocomposites studied and developed by Niihara and co-workers (1). Some composites have been obtained by dispersing nanoscale particles of SiC or Si3N4 inside or between the larger particles of Al_2O_3 or MgO matrix. In some systems, such as Si_3N_4-SiC nano-nano composites, superplasticity has been found.

Since the synthesis of SiC and Si_3N_4 by Haggerty and co-workers (2), the production of nano-powders ii-em gaseous reactants by laser-driven reactions has become an innovative application of lasers in chemistry. Laser synthesis of ceramic powders offers numerous advantages compared to classic pyrolysis methods. The reactions are conducted in a confined, well-defined, wall-less zone with rapid heating and cooling rates and with fast reaction times (1 to 10 ms) which can be controlled by varying the flow rate of the reactant gases, the reactor pressure or the laser power density (3).

Silicon - based powders, SiC, Si_3N_4, Si/C/N composites, have been produced from the laser pyrolysis of gaseous mixtures : (SiH_4 - C_2H_2, (SiH_4 - NH_3), (SiH_4 - CH_3NH_2 or $(CH_3)_2$ NH) with or without NH3 excess. The as-formed powders can be amorphous or crystalline with a variable chemical composition depending on the synthesis conditions (laser power, cell pressure, flow rates, and relative flow rates of the reactant gases). Silane (SiH_4) can be replaced by some ternary compounds in order to lower production costs such as dichlorosilane (SiH_2Cl_2), $CH_3 SiCl_3$, and gaseous hexamethyldisilazane (HMDS): $(CH_3)_3$ SiNHSi(CH3)3. Recently, a Si/C/N liquid precursor $((CH_3 SiHNH)_n$ where n is 3 or 4) has been injected into a C02 laser beam in the form of an aerosol produced by an ultrasonic nozzle (4). Furthermore, recent progress in laser technology shows that high-power, continuous-wave, tunable C02 lasers are now available (5).

V. TECHNICAL DESCRIPTION

V. A. POWDER SYNTHESIS (CEA)

We describe here a technique developed for the synthesis of nanometric Si/C/N composite powders using the interaction of a C02 laser beam with an aerosol of organosilicon liquid precursors. This technique has been extended to the synthesis of Si/C/O nanocomposite powders using liquid alcoxysilanes and a tunable C02 laser. We present the evolution of the as-formed powders (chemical composition and structure) after heat treatments up to 1600"C under nitrogen and/or argon atmosphere.

1. Experimental procedure.

1.1. The choice of the precursor.

In the case of (Si/C/N) nanocomposite powders, the liquid precursor, HMDS, was selected from investigations based on costs of various silicon precursors for the delivery of large quantities (> 1 ton/year) (Table I). Trichlorosilane (SiHCl3) and chloromethylsilanes are inexpensive; however, they unfortunately present no IR absorption band in the 9-11 μm wavelength region. They lead to SiC formation through endothermic reactions, whereas it has been shown that powder laser synthesis is favored in the case of exothermic reactions. HMDS, cheaper than SiH4 and producing a strong 10.6 μm absorption band was thus selected. Niihara and co-workers (1) used it for the synthesis of (Si/C/N) powders.

**Table I Investigation of some silicon precursors**

Formula	Molecular weigt	Boiling point (°C)	Silicon content (wt %)	Price Us. $ (Kg)*	Price u. s. $(Kg of Si)*
SiH$_4$	32.1	-111	87.5	300	343
SiH$_2$Cl$_2$	111.0	8.4	25.2	120	476
SiHCl$_3$	135.5	32	20.7 '	6.2	30
(CH$_3$)$_2$SiHCl	94.6	36	29.7	5.6	18,9
CH$_3$SiHCl$_2$	115.0	41	24.4	4.8	19.5
CH$_3$SiCl$_3$	149.5	66	18.8	2.4	12.6
(CH$_3$)$_2$SiCl$_2$	129.1	70	21.8	2.7	12,5
(CH$_3$)$_3$SiCl	108.4	57	25.9	3.1	11.9
SiCl$_4$	169.9	57	16.4	3,1	18.6
Si (CH$_3$)$_4$	88.2	26	31.8	N A	NA
HMDS$^+$	161.5	125	34.8	15	43.1

* Prices obtained during Summer 1992. From Hüls-France. Puteaux. France : S.A.F. Bulk Chemicals. Mulhouse. France : Praxair S.A. Rungis. France : and Alphagaz Bois d'Arty.France. with the following exange conditions : 1 U.S. $ = 5 FF = 1.47 DM. Not available in large quantities.
+ Hexamethyldisilazane.

(Si/C/O) composites were obtained from organosilicon liquids with a variable O/Si ratio and general formula $(CH_3)_xSi(OC_2H_5)_{4-x}$ with $0 \leq x \leq 3$ and hexamethyldisiloxane (CH3)3SiOSi(CH3)3). Their cost is in the cost range of HMDS. They present infrared absorption band in the 9 -11pm region.

1.2. **Experimental device.**
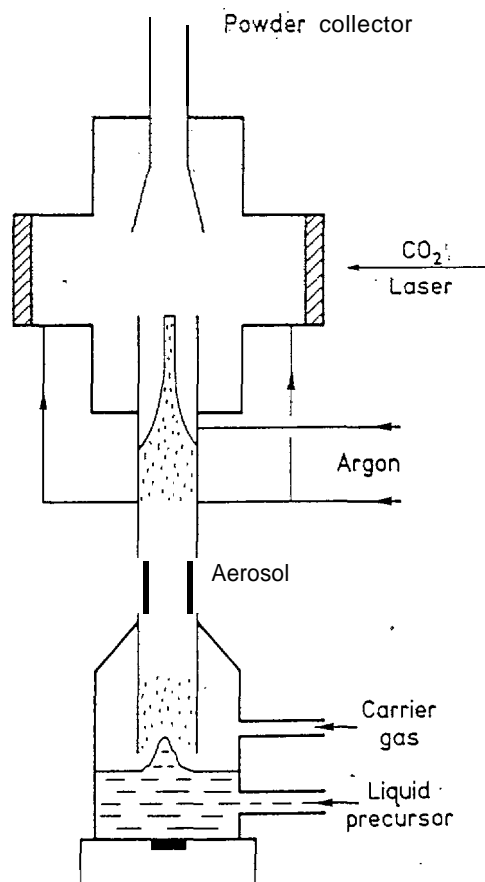
Fig1 Schematic of the aerosol generator with the irradiation cell

The experimental apparatus is shown in Figure 1, The liquid precursor was placed in a glass jar containing a piezoelectric transducer (Pyrosol 7901 type, from RBI). Focusing an intense beam of ultrasonic energy near the liquid surface yielded uniform droplets whose diameter d is given by:

$$d = 0,34 \left[\frac{8\pi\sigma}{\rho f^2} \right]^{1/3}$$

where o- and ρ are the surface tension and density of the liquid, respectively, and f the frequency of the transducer (850 kHz in this case). The aerosol droplets were injected through a glass inlet tubing (8. 8 or 13 mm) into an irradiation cell maintained at a regulated pressure of 1 atm using a flow of (argon-NH_3) mixture or pure argon for (Si/C/N) and (Si/C/O) respectively.

Synthesis experiments were performed with two high power fast axial flow CO_2 lasers. The model CI1 000 from CILAS-Alcatel, working at 10.6 μm with a 600W incident power was used for (Si/C/N) powder synthesis. The model 1500W from PRC-Oerlikon , in which a grating has been incorporated by RADIUS ENGINEERING to make it tunable in the 9-11 μm range, was used for (Si/C/O) powder synthesis. For the latter, figure 2 shows the power repartition between the emission lines.

POWER VERSUS WAVELENGTH AT 38 MA
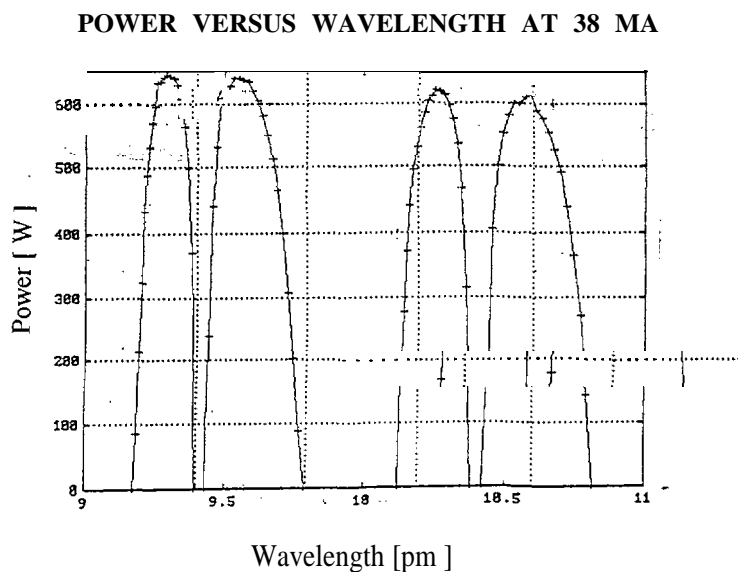
Fig. 2 **Spectral characteristics of tunable PRC OERLIKON laser**

The powders were collected in a glass chamber equiped with a cylindrical, stainless-steel filter and then maintained under argon atmosphere in a glove-box. Heat treatments under flowing argon or nitrogen were monitored up to 1600°C in a high-temperature graphite furnace at a rate of 600 °C/mn. .

As-formed and annealed powders were characterized by quantitative chemical analysis, IR spectroscopy, transmission electron spectroscopy (TEM), nitrogen absorption-desorption (BET) and X-ray diffractometry (XRD).

2. Results and discussion.

2.1. Si/C/N composites.

The synthesis experiments, here reported were conducted with a heated (100 - 110°C) liquid precursor in order to increase the quantity of liquid displaced. Synthesis results and chemical composition of as prepared powders are presented in Table II.

**Table II. Synthesis conditions and composition of the as-formed Si/C/N powders.**

Run or sample	Flow rates (cm^3/min)	Liquid displaced	Powder production	Powder/ Liquid yield	S_{BET}	Chemical analysis (wt%)				C/N atomic ratio
	Ar NH$_3$ Total	(cm^3/hr)	(g/hr)	(%)	(m^2/g)	Si	C	N	O	
HMDS 40	1935, 205 2140	182	59	43	110	46.7	25.3	21.8	6.1	1.35
HMDS 41	1770 410 2180	160	61	**50**	93	46.1	20.5	25.2	6.7	0.95
HMDS 42	i570 600 2170	175	75	**56**	98	44,4	18.5	29.7	7.7	0.73
HMDS 43	1370 800 2170	179	74	**53.**	95	44.6	15.5	26.8	7.7	0.67
HMDS 44	1150 1040 2190	**210**	8 1	**51**	95	46.6	12.6	22,3	10.7	0.57
HMDS 45	830 1350 2180	167	66	**52**	106	48,0,	7,7	25,0	11.6"	0.33

Powder production rates up to **80 g/h** have been obtained with a conversion rate (powder / displaced liquid) greater than 55%. The carbon content decreases from 25.3 (HMDS 40) to 8.3 wt% (HMDS 45). It is correlated with the NH3 content in the carrier gas. The nitrogen content change is less pronounced. The as-formed powders are amorphous. They present a specific surface area, greater than 100 m^2/g. This high value is confirmed by TEM which shows grain size in the range 20-30 nm (Figure 3). Some H bonds appear on the infrared spectra, corresponding to hydrogenated species.
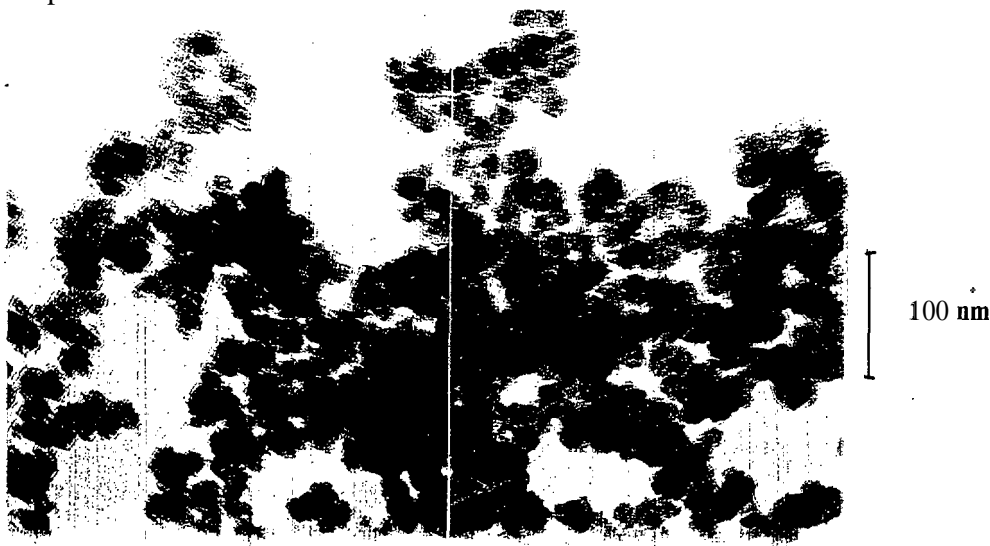
Fig. 3 **Microphotography of an as-formed Si/C/N** ex HMDS **as formed powder**

Figure 4 a shows the evolution of the chemical composition with annealing temperature. For an initial C/N atomic ratio in the range 0.5 -0.7 the chemical evolution toward SiC or Si3N4 appears at higher temperature compared to powders with higher or lower C/N, Figure 4 b shows that at 1600°C a straight change in composition occurs for the value C/N = 0.75 corresponding to the composition 3 SiC - Si3N4 , which is also the composition of the tetrahedron SiC2N2.
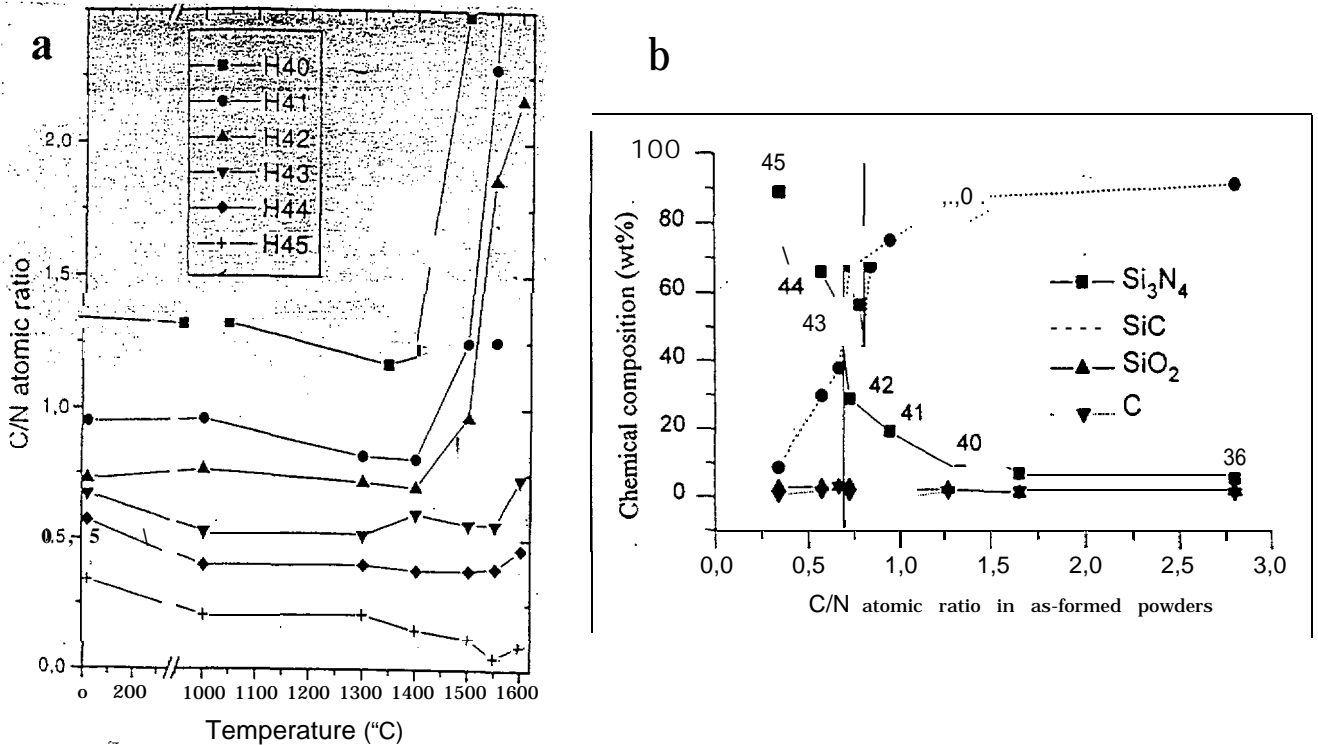
Fig.4. (a) Evolution of C/N atomic ration with annealing temperature. (b) Phase proportion after heat treatment: 1600°C / 4 h / N2

2.2. Si/C/O composites.

Synthesis experiments are performed with liquids at room temperature and the production rates are in the 20 - 40 g/h range. The calculated chemical composition of the as-formed powders, summarized in Table III, are deduced from the chemical analysis, assuming that oxygen is bonded to silicon and the remaining silicon to carbon.

Table ICI. Composition of the as-formed Si/C/O powders

Precursor	Sample	Chemical analysis (wt %)			Calculated chemical composition
		C	O	Si	
$Si(OC_2H_5)_4$	TEOS	2.1.1	41.8	35.1	$SiO2 +$ 1.4 C
$CH_3Si(OC_2H_5)_3$	MTOS	27.0	36,6	32.4	$SiO2 +$ 1.94 C
$(CH_3)_2Si(OC_2H_5)_2$	EOMS	28.3	34,0	35,3	$SiO2 + 0.19$ SiC + 2.04 C
$(CH_3)_3SiOC_2H_5$	ETMS	29.4	28,3	42.4	$SiO2 + 0.71$ SiC + 2.05 C
$[(CH_3)_3Si]_2O$	MDSO	29.9	16.7	50.7	$SiO2 + 2.45$ SiC + 2.30 C

These compositions are in good agreement with IR spectra. SiC formation occurs for EOMS, ETMS and MDSO samples. It is related to the O/Si atomic ratio of the precursor (O/Si < 2); it increases with the number of C-Si bonds in the precursor formula. C content increases with the number of methyl groups. These initial compositions induce transformations in powders after annealing.

Table IV. Evolution of Si/C/O powders on annealing

PRECURSOR	Characterizations of Si/C/O powders after annealing under argon							
	Ar, 1300°C, lh				A r , 1500°C, 1h			
	C (wt%)	O (wt%)	Am (%)	S_{BET} $(m^2.g^{-1})$	C (wt%)	O (wt%)	Am (%)	S_{BET} $(m^2.g^{-1})$
TEOS	16.0	39.7	n.m.	85	2.5	53.6	-22.9	0.1
MTOS	26.5	34.7	-24.1	242	26.6	8.6	-74.1	*
EOMS	25.5	32.7	-30.0	173	28.8	n.m.	-75.0	20
ETMS	26.9	21.5	-24.8	102	29.3	4.8	-49.3	25.5
MDSO	28.8	15.5	-38.0	70	27.5	5.3	-33.7	36.5

After oxidation under air, silica powders with high specific *surface area* (**400 -500** m^2/g) and with low C content (O. 1-0.2 wt%) are obtained for MTOS and EOMS samples. No morphology change was observed by TEM for MTOS sample. Increase in specific surface (S_{BET}) value is attributed to porosity formation after oxidation of the very fine C particles. The specific surface area remains high up to 900°C.

After annealing under argon, mixtures of SiO2, SiC and C or SiO_2/SiC/C composites are formed. The Si/C/O composite powders obtained after firing at 13 OO°C are in the nanometric range as confirmed by BET measurements. At 1500°C, excepted for TEOS sample which coalesces in silica grains, the S_{BET} value remains high. At 1600°C the S_{BET} value decreases abruptly with coalescence.

3. Powder pelletisation.

The as-prepared flocky nanopowder is difficult to handle. Conditioning is necessary before processing. Two ways have been experienced: suspension in a liquid and pelletisation.
Suspension of (Si,C,N) nanopowders cannot be made in acetone, which has been proved to be the best "dispersing medium, over a concentration of 10 g/1. Beyond this limit, the powder agglomerates and settles down. No dispersent happened to be efficient. On the other hand, suspension in water with few percents of dispersent brought the limit to 100 g/l. Beyond, the viscosity of the suspension increases dramatically.

Pelletisation has been achieved from an aqueous slurry. Spray drying resulted in 20 to 40 microns granules. Oxidation occuring during this process happened to be reversible as the extra oxygen concentration (typically 3 -4°/0) steps down after one hour of a dewaxing heat treatment at 800°C in hydrogen atmosphere.

As a conclusion for nanopowder synthesis and handling: the presented results illustrate the versatility of the laser technique. The caracterisation of the powders in relation with operating conditions of the laser reactor, as well as the understanding of their transformation during heat treatment brings about a useful knowledge for a subsequent development.

V.B. POLYSILAZANE PRECURSORS SYNTHESIS. (ELF ATOCHEM).

At the beginning of this project, Elf Atochem was developing polymeric precursors of silicon carbonitride : polysilazanes (polysilylhydrazines) .One of them, Pyrofine PV, liquid at ambient temperature exhibits relatively low viscosities upon heating (20 mPa. s at 150°C), and was used to infiltrate ceramic fibers preforms to make ceramic-ceramic composites. It has therefore been proposed as a candidate for the flash pyrolysis of fine droplets to obtain nanocomposite powders.

However, the main difficulty faced during this project has been a too high viscosity of Pyrofine PV. Ideally, 1 mPa.s at room temperature was desired for the ultrasonic probe used to generate the spray. Three research axis have been explored.

1- Synthesis of a less visquous polymer

The basic polymerizations being based on reactions between chlorosilanes and hydrazine, a proper choice of the combination of chlorosilane monomers allows to reduce the chain lengths and the associated viscosities: the higher the chlorine atoms content in the monomer, the higher the lengths and branching. Several laboratory trials were run, and one of the products has been produced in a small pilot reactor (reference TVP 54/55). The viscosity was reduced down to 38 mPa. s at 25°C and 8.5 mPa.s at 70°C. This product as well as the laboratory scale ones have been fully characterized (chemical compositions, thermal behaviour, impurities).

2- Heating up during the ultrasonic spraying

Heating up of these polymers reduces the viscosity. CEA made some trials either with Pyrofine PV or with TVP 54/55. TVP 54/55 behaved better than Pyrofine PV. Some technical problems occured regarding the use of the ultrasonic probe at high temperatures.

3- Dilutions of the polymers by low viscosity silicon-based monomers

Hexamethyldisilazane (HMDS) was selected as a first candidate to dilute the polymers, since HMDS is already converted with a low yield to ceramic during the laser flash pyrolysis.

Addition of 40 % of HMDS drastically reduces the viscosity at room temperature down to 10 mPa.s for Pyrofine PV and 4 mPa.s for TVP 54/55. Dilutions of 50 % have been tested by the CEA, and allowed to obtain a very fine silicon carbonitride nanosize powder. But the system could not be very stable due to high consumption of diluant.

In the meantime a comprehensive work based on the reactions taking place during pyrolysis was performed. Several diluants have been tested, and tetramethyl disilazane (TMDS) was found the most efficient to lower the viscosities and increase the ceramic yields.

In conclusion, the polysilylhydrazines, already available from Elf Atochem or developed in the frame of this project, had too high viscosities for the ultrasonic spraying. However, it has been demonstrated that nanocomposite powders could be obtained from these precursors by laser flash pyrolysis. Further development would necessitate to design a new droplet generation device.

V.C. TUNGSTEN CARBIDE NANOPOWDERS. (CERAMETAL)

Tungsten carbide nanopowders have been experimented for cutting tools applications.

Laser synthesis of ultrafine WC powders has been tested from gazeous (WF_6) and liquid (WCl_6) precursors. Only the previous one gave results. Sulfurhexafluoride is added as an absorbant of the laser radiation. The reaction is the following:

$$2 WF_6 + C2H2 + 5 H2 + (SF_6) ------> 2 WC + 12 HF$$
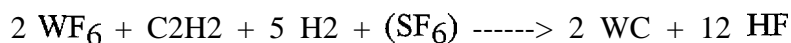
The powders collected are dark, they contain several percents of sulfur and fluorine based compounds. The as formed powders fix up to 8-10 wt % of oxygen, leading to a poor-defined oxycarbide structure. A specific surface of 100 m2/g has been measured.

Several heating experiments have been made to eliminate these impurities and to form stable nanocristallised WC powder. To name few results:

- air oxidation of the powders up to 750°C leads to W03 formation and decrease sulfur content below 50 ppm. But some noticeable grain growth cannot be hindered.

- under neutral conditions (argon), the different steps of the (W,C,O) compound decomposition have been identified and nanometric WC powder has been formed, with still high specific surface area (# 85 m2/g). However, the residual sulfur content has never been decreased under 0,1 O/O; even under firing temperatures in the 1300- 1500CC range. Difficulties in complete removing of sulfur may arise from tungsten sulfide presence in the powders.

- further elimination of sulfur could be achieved in H2/Ar atmosphere to form volatile H2S, since outgassing of H2S has been observed up to 11 00°C. However, carbon loss in H2 have impeded WC formation.

At the present state, the remaining sulfur content is too high, regarding the specifications for usual submicronic WC powders aiming a cutting tool applications.

V.D. EROSION RESISTANT COATINGS (SNECMA)

Erosion is one of the main failure mode of compressor blades in aero-engines. It seems that a good resistance should be given by using a ductile coating, alloyed with hard particles, these particles being of a smaller diameter than the eroding ones.

A sequence of deposition has been found, in order to build up a coating having a good adherence, a minimum porosity and an homogeneous repartition of the ceramic particles. The different steps are listed below:

  1. blasting of the support surface
  2. electrophoretic coating of nano SiC in (nitromethane / isopropylic alcohol) with SiC concentration of 9 g/l. Thickness of the coating: 12-15 microns. Charge of SiC nanoparticles on the surface: 2 mg/cm^2.
  3. electrochemical coating of nickel using nickel lactate, pH 7-
  4. electrochemical consolidation with cobalt, using sulfamate solution, pH 4. The sequences 2 to 4 are reconducted 2 or 3 times.
  5. thermal ageing during 6 hours at 600°C under vacuum
  6. tribofinish, in order to eliminate superficial SiC and to obtain surface smoothness,

A good dispersion of SiC particles and metallic Co or Co/Ni reinforcement at 100-200 nm scale has been demonstrated by microscopic analysis and X ray-electron spectroscopy. Standard tests of sand erosion have shown a definite resistance to damage. But the economic cost of this protection is in question.

200 μm
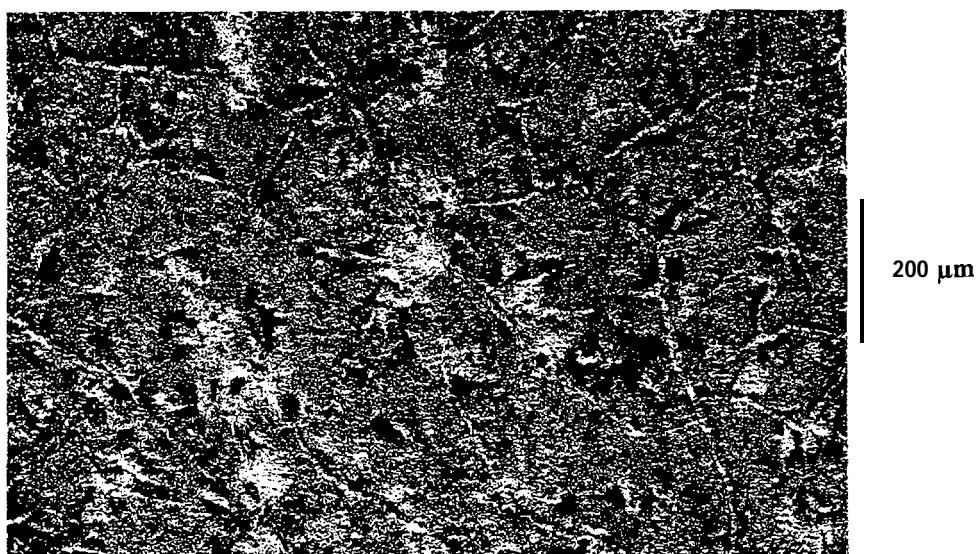
Fig. 5 A typical surface view of a SiC/Ni deposit

V.E. SINTERED CERAMICS. (VITO).

1. Introduction

One of the objectives of this project was to explore the potentialities of laser synthesised nano-size powders as raw materials for manufacturing monolithic advanced technical ceramics and to evaluate their impact on the properties of the sintered material, Nano-SiC, containing sintering additives B and free C readily from synthesis, and nano-SiCN have been studied.

Laser synthesised powders consist of 10 (in the case of SiC) to 50. nm (in the case of SiCN) monomodal spherical particles which are highly agglomerated in long branched chains, resulting in very low packing efficiency. TEM observations show often necks between the particles illustrating the high strength of the agglomerates and the difficulty to shape such powders into green compacts. If one wants to study the intrinsic material properties after shaping and sintering the main emphasis should go to processing. Indeed, as long as defects such as stacking faults

resulting from inappropriate processing persist, the mechanical behaviour of the material will be determined by these defects, thus concealing the real material properties.

Another issue is the high tendency of non-oxide nano-powders to oxidise when exposed to ambient air or humid atmospheres. This tendency is related to the high surface area of the powders. The oxidation mechanism seems to be hydrolysis by moisture. It has been shown for nano-SiC powder that an equilibrium oxygen content is reached proportional to the relative humidity of the surrounding atmosphere.

2. **Technical description**

Taking into account the above considerations all powders have been handled in glove boxes under dry nitrogen. The main emphasis was put on developing proper processing methods. Powder conditioning of nano-SiC consisted of water free wet milling, drying or preparing suspensions by ultrasonication. In the case of SiCN the powders were thermally treated and used as amorphous powders or crystallised. Some crystallised material has also been processed in water and freeze dried. Sintering additives Y_2O_3 and Al_2O_3 were added as ceramic powders or as a colloidal suspensions of nano powder. Components were shaped by uniaxial compaction, cold isostatic pressing or pressure casting. The material was then pressureless sintered using different types of powder bed protection, gas pressure sintered or hipped. Optimum sintering conditions were determined by a statistical approach. The material was characterised by density measurement, optical and transmission electron microscopy, phase composition analysis by XRD and microprobe analysis. From these a workable processing route, resulting in dense composite components, could be put forward.

3. Results

Nano-SiC

Nanosize SiC powder, containing B and free C as sintering aids from synthesis, can be processed into full dense material by pressureless sintering. Compared to conventional powders the nanopowders shows a much higher sinterability. Unfortunately grain coarsening during sintering results in a final microstructure similar to that obtained with conventional powders.

Nevertheless, the co-synthesis of the sintering aids makes them much more effective. Due to the homogeneous distribution of the additives the total amount of B and free-C can actively play its role: reducing the oxygen present in the powder and suppressing surface diffusion, the origin of grain growth, in favour of volume diffusion, the driving force for densification. In contrast to conventional powders a stochiometric free-C/O ratio is sufficient to suppress premature excessive grain growth. In this way it is possible to produce sintered SiC without excess graphite as a secondary phase.

In an attempt to master the grain growth in order to keep a nanostructured material after densification the same material has been densified by encapsulation hipping. Applying very low temperatures (1450°C) and long sintering times (8h) densities above 90%TD have been obtained without grain growth. It is believed that in this way higher densities can be obtained, if pure SiC material is used instead of the B-doped SiC synthesised specially for pressureless sintering. Indeed it is known from experiments with conventional powders that full densification by encapsulation hipping is hindered by the presence of B.

Contrary to monolithic SiC were grain growth can destroy the nanostructure, in composite materials the particles of the second phase are separated by the matrix. Even if during sintering the grains of the matrix phase grow it was hoped that the isolated particles of the second phase should remain nano-size. It worked out that this is only true to some extend. Si_3N_4 is sintered by a mechanism of solution in and precipitation from a liquid phase formed by the sintering additives. It has been recently shown that SiC can also be sintered by the same mechanism. Thus, although Si_3N_4 and SiC are nano-size after powder conditioning, at least part of the SiC will also grow during liquid phase sintering. Under the conditions of pressureless sintering to high density the resulting material consists of typical elongated Si_3N_4 grains and homogeneously distributed equiaxed sub-micron SiC grains. Only part of the SiC is found as an intergranular nano-phase inside the Si_3N_4 grains.

4. Conclusions

Pressureless sintered nano SiC has a microstructure similar to conventional material due to grain coarsening during sintering. Nevertheless the co-synthesis of sintering aids results in a much more homogeneous distribution of the B and free C. Such a powder is less vulnerable to excessive grain growth and can be processed into sintered SiC without excess C as a secondary phase.

It is believed that dense nano structured SiC can be obtained when nano SiC powder without sintering additives is encapsulation hipped for long times at temperatures as low as 1450°C.

Amorphous ex-HMDS powder with a C/N ratio lower than 0.75 can be converted into high density composite material applying proper processing. Depending on the starting powder and on the sintering conditions SiC reinforced Si_3N_4 composites containing 10 to 40°/0 SiC have been obtained. The material consists of a matrix of typical elongated Si_3N_4 grains in which most of the SiC is homogeneously distributed as submicron particles. The rest of the SiC is present as a nanometric intergranular phase inside Si_3N_4 grains. Further work is needed to correlate these structures with material properties.

VI. RESULTS.

. The laser synthesis of silicon containing nanopowders was realised from inexpensive liquid precursors; namely, hexamethyldisilazane for (Si,C,N) and hexametyldisiloxane for (Si,C,O). Their low viscosity made them able to be injected by nebulisation into the laser irradiation cell. However, it was demonstrated that more viscous polysilazane can lead as well to nanopowders as far as an adapted dropwise injection is conceived.

. A tunable laser in the range 9-11 microns was used for (Si,C,O) powders synthesis.

. Tungsten carbide nanopowder was prepared for cutting tools applications. The precursors of tungsten carbide were tungsten hexafluoride and acetylene. Small amounts of sulfurhexafluoride were added for sake of photo absorption. But attempts to get rid of the remaining sulfur did not succeed in lowering the sulfur level below 20 ppm, which is compulsory to sinter such hard metalcarbides.

. Erosion resistants coatings have been elaborated in the form of silicon carbide dispersion in a metal matrix composite. Dispersion of SiC particles in the Ni or Co metal matrix is close from 100 nm level. A two step process was worked out: electrophoretic deposition of SiC consolidated by electrochemical deposition of the metal. The mechanical stability of the deposit dictates to limit its thickness below ten microns. Three layers must be deposited in order to reach an appropriate thickness of 20 microns. A significant resistance to silica dust impact has been demonstrated.

. Dealing with sintering of nanopowders, a considerable knowledge has been accumulated on how the nanopowders of SiC and (Si,C,N) must be processed, namely: powder conditioning (degazing, pre-cristallisation), dispersion of sintering aids, samples fabrication, sintering in various conditions (temperature, pressure, atmosphere). Densification over 95°/0 has been obtained with the help of aluminium and ytrium oxide additives. The overall problem lies in promoting densification while preserving a fine crystalline structure. Practical answers related to process conditions are now available.

VII. CONCLUSION

The results presented in this report demonstrates the possibility to produce silicon containing nanopowders available for applications. The production, at the moment, is still at a laboratory level. But the CEA team have precisely located the technical points which could enhance the laser productivity. The production could reach, at a pilot scale, 1 kg/h or 2 T/an. This seems to be sufficient to satisfy a formless incipient industrial market.

Its worth to know that, at the present time, (Si,C,N) powder cost is 1000 dollars/kg. At a pilot scale this price could be lowered to 200 dollars. The most often reported figure for a material involved in a high tech application, with a low diffusion, lies between 20-40 dollars/kg. Such a price could be only attainable in the case of a connected production of more than **50** lasers. Probably the laser technique will have to face others possible candidates. At the present time, we can not tell which one will be the most attractive in terms of particles dimensions, purity and productivity.

It can be concluded that an additional period of 2-3 years is necessary to identify eventual emerging application. At the present time we can assert that an intermediate laser pilot production fits the present industrial needs for R&D. The partners of the present project maintain among them a consortium type of relation in order to help any development based on the nanostate of the materials.

VIII ACKNOWLEDGEMENTS

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