On Line Characterization of SiC Nanoparticles Produced by Laser Pyrolysis

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Abstract. On Line Measurements campaigns have been carried out for the first time in IRAMIS/SPAM CEA’s laser gas-phase pyrolysis nanoparticles production facilities. The produced aerosol is composed of Argon and/or Helium laden with SiC nanoparticles concentrated up to ~14 mg/l. Different commercial apparatus were used for sampling, and characterisation of size, and morphology of the particles. A series of experiment is performed by IRSN with a DMS500 from Cambusion Ltd™, which gives electrical mobility equivalent diameter distribution in real time. Particles are sampled with an ejector-diluter VKL-10 from Palas™. On the same sampling line, APTL performed aerodynamic equivalent diameter mass distribution using a Nanomoudi from MSP Corp.™ and TEM post analysis, as well as post elemental analysis (EDS) after collection on TEM grid with a Thermophoretic Precipitator (TP). A previously developed model is used to obtain the aggregate morphology and primary particles sizes. In addition to these commercial or well-known techniques, a new patent-pending technique called RFPM (Radio Frequency Plasma Metrology developed by CILAS + GREMI in the frame of NANOCARA program) is tested for the first time off the lab. The principle is based on levitation of particles in plasma RF. The entire set up is a prototype, including the sampling line. Experiments showed that this technique is very promising for on line gas phase monitoring, even though future improvements are needed, especially on the direct injection of the sample in the measuring chamber.
First results of size distribution on pyrolysis line were obtained: three modes of different geometric mean diameter D50 were measured. Further analysis of TEM micrographs gave insight on these three modes, they can be interpreted as primary particles, aggregated particles, and a third one which could be composed of silica oxide nanoparticles issued from the combustion of the remaining silane initiated by an air leak in the exhaust of the reactor. Furthermore, a parametric study was undertaken. Helium addition in reactor and laser power were authorized to vary within a significant range. There was an evidence of influence of these parameters on the size distributions.

Thus, we have demonstrated the high interest of implementing a size monitoring set up on gas phase nanoparticles production line for safety, yield improvement, and cost reduction purposes. This set up can run in a safe and non invasive way, and require low maintenance.

1. Introduction

The worldwide consumption of nanomaterials was estimated at more than 10 millions of tons and its annual growth is evaluated at 2.7% in volume in 2006 [1]. Their domain of interest coincides with the emergence of research activities like biomedical, food packaging, coatings or new surface properties, energy, and catalysis applications. The manufacturing of nanoparticles opens new economical developments as well as highlights a social concern about their control.

One may distinguish two kind of technique for nanoparticles elaboration: Liquid-phase and Gas-phase. We focus on the second one. Gas-phase nanoparticles manufacturing is nowadays widely employed. A topic of annual Aerosol Conference (European and International) is dedicated to this [2]. Major benefits of this technique can be summarized as:

- High chemical purity (no surfactant, purity of the gas)
- Continuous operation, high throughput (in the order of kg/h).
- Low waste of chemical, solvent, or other products = low environmental impact, cost effective, large scale production.

The most widely used gas-phase manufacturing techniques for mass production are based on heating (vaporization, cracking) and cooling (condensation, coagulation) process steps: Hot wall furnace, flame, spark-discharge, plasma, or laser pyrolysis can be cited as the most representative techniques [3].

The size and aggregation state of the nanoparticles is a crucial parameter regarding their properties and process control (for development, as well as for routine production). Monitoring this parameter On Line is of prime importance to achieve a high-yield, safe, and reproducible mass production.

Up to now, the best techniques for size distribution and counting nanoparticles in gas phase in real or quasi real time are:

- Electrical mobility spectrometers: Scanning Mobility Particle Sizer (SMPS) [4], and Differential Mobility Spectrometer (DMS) [5].
- Aerodynamic equivalent diameter: Electrical Low Pressure Impactor (ELPI) [6].

The major drawback of these techniques is that they show limitation in continuous operation on a production line at high concentration values. Indeed, whatever the technique, clogging, deposits on sensors or other parts cause a drift or malfunction. Maintenance is then necessary at interval period of the order of hours, which is not compatible with continuous process operation.

Thus, reliable, low maintenance, secure, and non invasive technique for continuous real time size measurements has to be developed.

Development of innovative techniques for Gas-phase On Line characterization tools is the main objective of NANOCARA program [7]-[8], which is currently in progress. In the frame of this program, a new patent-pending technique for particle sizing is being developed. We will not give details the principle of operation, for confidentiality reasons.

This innovative technique has been successfully tested in the lab with micron and submicron particles [9], but never on a gas-phase nanoparticles production line. The complementarities between NANOCARA and SAPHIR goals were an opportunity to assess this technique in parallel with other established ones. Therefore, the work presented in this paper is carried out in the frame of SAPHIR
program, which aims at implementing direct production of nanoparticles through the development of a
global integrated concept, with safe oriented processes, and global monitoring strategy.

The objective of this paper is to report the two measurements campaigns performed at
IRAMIS/SPAM CEA Saclay at different time:

- CILAS and GREMI: integration of RFPM prototype device on the pyrolysis line. Sampling
  and size distributions measurements for nominal synthesis conditions. A few series of
  measurements with laser power variation and helium addition in the reactor were done.
- IRSN and APTL: counter measurements with DMS500 Cambustion Ltd™, Thermophoretic
  Precipitator for TEM analysis, and Impactor NanoMoudi MSP Corp. ™. These measurements
  were carried out with the same synthesis conditions, and parametric variations.

2. Experimental set up

2.1. Overview of experimental set up

![Experimental setup diagram]

**Figure 1.** Overview of the experimental set up installed on line.

**Table 1.** Sampling parameters. DMS500, Nanomoudi, and TP were installed on
the same sampling line simultaneously, with a flow splitter (section 0). RFPM
was operated at a different period (section 2.4.).

| Sampling | DMS500 | Nanomoudi | TP | RFPM |
|----------|--------|-----------|----|------|
| Flow Nlpm| 8      | 8.2-9.2   | 3.5-4.1 | 0.15-0.7 |
| Duration | Contin. | 15-20 min | 7-9 min | 60 - 90 s |
| Dilution ratio | 62:1 | 62:1 | 62:1 | 2:1 - 10:1 |

**Table 2.** Pyrolysis parameters. During experiments campaign, a parametric
study of fundamental parameters has been carried out.

| Laser power | Helium dilution |
|-------------|-----------------|
| 10 - 30 % of F.S. (*) | 0 - 40% of F.S. MFC (F.S = 3.5 Nlpm) |
| 180-540 W | |

(*): F.S. = Full Scale
2.2. Laser Pyrolysis technique
Laser pyrolysis is a gas phase process currently used for the synthesis of various kinds of nanoparticles [10]. It is based on the resonance between the emission of a laser, usually a CO$_2$ laser at 10.6 µm, and the absorption of a gaseous (or liquid) precursor molecule. In this thermal process, the CO$_2$ laser is used as an easily adjustable heat source for the precursor molecules collision-induced decomposition. The precursor’s flow, guided by a coaxial inert gas flow, intersects orthogonally the laser beam in a reaction chamber kept under controlled pressure. The temperature increases rapidly in the laser-crossing region. If the particle formation temperature is reached, nucleation takes place from dissociated species and particles are growing rapidly. The reaction zone shows a luminescent flame originated by the thermal emission of the particles and possible emission contributions from excited radicals. The confinement by the inert gas flow avoids any reaction with the chamber walls and thus prevents particles from pollution.

Nucleation and growth processes in laser pyrolysis show some similarities with those observed in combustion flames. Both methods essentially differ in the way precursor molecules are dissociated. This may lead to the formation of different chemical intermediate species and/or different electronic energy states of these species. Chemical reactions that are involved at least in the beginning of the process may then have different pathways. Particles grow either by atom addition to their surface induced by vapor flow condensation or by chemical heterogeneous reactions on their surface. If the temperature is sufficiently high, coagulation can occur simultaneously. In that case, particles are growing by melted particle-particle collision or by solid-state diffusion between two hot solid particles. Primary particles may agglomerate or aggregate in larger fractal-like objects. The growth process, the primary particle size, structure and the agglomeration degree are strongly influenced by the synthesis parameters such as precursor molecules flow, pressure in reaction chamber and laser intensity. In addition to these usual parameters, it is possible to dilute the reacting precursor flow.

2.3. IRSN + APTL sampling and characterization set up
Nanoparticles were sampled in the exhaust duct of the pyrolysis reactor with an ejector type dilution device (PALAS™ VKL 10) fed with nitrogen for inerting the remaining silane. Prior to sampling, a dilution ratio of 62:1 was measured using two thermal mass flowmeters (4043 TSI™). The size distribution was determined continuously in terms of electrical mobility diameter using a differential mobility spectrometer (DMS 500 Cambustion Ltd.) and in terms of mass aerodynamic diameter according to a substrates sampling (aluminum foil) of 15-20 min with a rotating micro-orifice impactor NanoMoudi (MSP Co.™). The size range covered by these two spectrometers was respectively from 5 to 1000 nm for the DMS 500 and 10 nm to 10 µm for the NanoMoudi. Nanoparticles have been also deposited on electronic microscopy grids (Formvar and Holey carbon) using a thermophoretic precipitator developed by APTL [11]. In parallel to the size distribution, the morphology and chemical composition have been investigated on grids by transmission electronic microscopy [11], energy dispersive spectroscopy and on NanoMoudi samples by x-ray diffraction.

The morphology of collected nanoparticles samples is studied via TEM image analysis in order to extract important structural information such as: (i) the primary particle distribution (Dpr), (ii) the equivalent projected area diameter (Dea) distribution of the aggregates, which relates straightforward to the corresponding mobility diameter (dm) distribution, (iii) the fractal dimension (Df), (iv) the fractal prefactor (kg), (v) the coefficient of overlap (Cov) in-between primary particles, that leads to an estimation of (vi) the depth of penetration (dij) and, finally, (vii) the fill factor (f(Cov)).
2.4. RFPM set up

2.4.1. RFPM brief description. This new device is now patent pending [12], thus the operating principle cannot be described here in details. This technique takes advantage of the low pressure and power plasma RF as follows:

- Levitation of particles in plasma allows trapping of particles.
- De-agglomeration of particles weakly bonded (Van der Waals) in dry phase.
- Low pressure mobility of particles is high even for nanoparticles.

Figure 3 shows a CAD view of the main parts of the prototype in-house device that was used for lab and On Line experiments. Other parts are described in section 2.4.2.

Particles to be measured are charged in the plasma by free electrons, the arising electrostatic force counterbalances the gravitational one, and thus lead to levitation of particles arranged in layers for diameters under approximately 10 µm depending on the material density.

The measured diameter could be related to a kind of Low Pressure Mobility equivalent diameter. At this range of pressure settling velocity of nanoparticles are high enough to be exploitable with reasonable time response (few seconds).

2.4.2. Sampling On Line. The sampling system used for experiments is a prototype made in the lab. The nozzle is Swagelok™ stainless steel tubing 4 mm internal diameter, and adjustable in position. It is adapted to an ISO KF cross, installed on the exhaust duct of the pyrolysis. The flow in the
instrument is controlled by a downstream critical orifice (500 µm diameter) set at 2 Nlpm of nitrogen at atmospheric pressure. Mixing ratio and sampled aerosol flow was adjusted by changing the setpoint value of the nitrogen mass Flow Controller. The flow of sample extracted from the line was controlled between 0.17 and 0.7 Nlpm, corresponding to mixing ratios between 2:1 to 10:1.

Temperature measurements in situ at the inlet of the instrument have been performed in these conditions. Temperature of the diluted aerosol never exceeded 25°C, which is compliant with RFPM device (no thermophoresis deposits in the chamber).

The sample to be measured is not directly injected in the plasma chamber, but thanks to a sequential injection technique. Particles (only a few milligrams or less) are collected in a tank at sampling pressure, then, the pressure is lowered by pumping with a dry primary pump to the working value (a few tenth of millibar). By means of actuation, the sampled particles are released in the low power Radio Frequency Plasma.

The main issue is the pressure adaptation: in fact, between two measurements, device must be blanked out to minimize memory effect due to remaining particles in the collecting tank after injection. Thus, the entire 4-steps sequence Sampling/Collection - Injection - Measurement – Blank leads to delay of approximately 15 minutes between two samples.

3. Results and discussion

3.1. Size and mode distribution

![Figure 4. DMS 500 size distributions for 30 % of laser power and various helium flow rates](image)

The size distributions measured in real time by the DMS 500 are presented on Figure 4 for 30 % of laser power and various helium dilution flow-rates. Three well defined modes can be identified on these size spectrums. The smallest one, close to 17 nm, is associated to the primary nanoparticles whose the diameter measured by TEM is in good agreement (cf. part 3.2). The largest mode (ranging from 194 to 340 nm) can be attributed to the nanostructured agglomerates observed by TEM (cf. part 3.2). Furthermore, a third intermediate mode (close to 69 nm) can be clearly identified but has not yet been fully described. This mode may be due to an air leak observed detected after the experiments. This leak may cause the combustion of the remaining silane and, as a consequence, a significant production of silica oxide nanoparticles. One must notice that a large amount of oxygen has been clearly identified on the EDS spectrum of nanoparticles (cf. part 3.2).
RFPM raw data consists of two signals coming from two sensors. Further calculations allow constructing the size distribution. This methodology is patent pending, and we will not explain it in details here. It is worth to note that hardware encountered a malfunction in the pressure recording during all the experiments. It is an important parameter, as it is used in formula for size calculation. Therefore, size distribution and median diameter $D_{50}$ (count median diameter mode) are calculated with an error of 20 to 30%, because pressure is set at 0.25 mbar for all data (this is the nominal value for each measurement, but manually adjusted and varying within ~20%).

Fluctuations of the signals are not artefacts (Figure 5). The resolution is very high. This is a strong advantage of the technique when multimodal and polydisperse populations are to be measured. Due to the hardware design and signal processing electronics (lab prototype version), S/N ratios are not optimized, especially in the range 10-100 nm.

It is worth to note that it is not a physical limitation of the technology RFPM. Hardware upgrade and sensor gains adjustments in the low diameter range can drastically improve the S/N ratio. In fact, the larger the diameter is, the larger is the measured signal, with a predictable function. Thus, this can be overcome by adjusting the gain of sensor response with respect to the diameter.

The RFPM size distribution corresponds to aggregate state of nanoparticles. Calculations give a $D_{50}$ between 135 nm and 185 nm for all conditions (Figure 6). $D_{50}$ values are not dependent on the injected and measured quantity.

The results obtained with the impactor NanoMoudi are expressing the mass of each size range as a function of the aerodynamic diameter of the particles. In the following figure (Figure 7), the results obtained from NanoMoudi at three typical points of laser pyrolysis operation (30%Laser - 0%He, 30%Laser - 20%He and 30%Laser - 40%He) are presented, expressed as the calculated number concentration $dN$ versus the average aerodynamic particle diameter $d_p$. SiC particle density employed for raw data assessment is 3.02 g/cm$^3$. 

![Figure 5. Example of RFPM calculated Size Distribution in normalized number. To statically improve the $D_{50}$ measurements, and mitigate noise influence, distributions are fitted with log-normal function. Thus, results are more reliable.](image)

![Figure 6. Significant RFPM $D_{50}$ (Blank / Signal ratio lower than 5%). X axis scale represents the experimental conditions. 30%/10% means CO$_2$ laser is operated at 30% of maximum power, and 10% = Helium flow-rate is set at 10% of full scale (cf. Table 2).](image)
3.2. TEM and EDS analysis
The samples collected on the TEM grids by the thermoprecipitator representing the whole size distribution of each experiment, as well as selected samples collected by NanoMoudi representing fractionated parts of the size distribution, were studied at the TEM microscope and several pictures are taken at various magnifications. Most of the samples that were studied at TEM were also analyzed by EDS (Energy Dispersive Spectroscopy) elemental analysis. In the following representative TEM pictures, important characteristics of the nanoparticles produced by laser pyrolysis are depicted, such as representative values of the primary particle size, the aggregate size and the number of the aggregates as well as representative chemical analyses in selected spots of the samples.

Figure 7. NanoMoudi results at three typical points of laser pyrolysis operation (30% Laser - 0% He, 30% Laser - 20% He and 30% Laser - 40% He)

Figure 8. Representative TEM pictures of typical point of operation 30% Laser-0% He

Figure 9. Representative TEM pictures of typical point of operation 30% Laser-20% He

Figure 10. Representative TEM pictures of typical point of operation 30% Laser-40% He
It is worth noticing that mainly Si, C and O were identified by EDS and in limited cases also N was identified. However, the quantities measured by EDS are really small and that is the reason why the EDS diagrams are produced after zooming a lot in the measuring range and therefore they are not of the highest quality.

3.3. Fractal analysis, primary particles and aggregate size distribution analysis

Image analysis was performed on samples collected from the impaction stage of NanoMoudi that corresponds to the aerodynamic range of 1000nm to 1800nm, while for each sample, the diameters of a satisfactory number (above 100) of primary particles were measured using high magnification images. The results are exhibited on the following table. For two of the samples it was found that the primary particles are following a bimodal normal distribution. For the rest of the analysis, the set of measuring quantities were the overall projected area (\(A_{agg}\)) and the length of the bounding box that could fully enclose the aggregate. From the equivalent projected area diameter \(D_{ea}\), \(A_{agg}\) was obtained for each aggregate. Those values were used to reconstruct the size distribution of the aggregates assuming that they follow a lognormal distribution. The overall results are summarized in the graph of Figure 11 and Table 3.

| Sample          | \(D_{pr}\) (nm) | \(D_{ea}\) (nm) | \(D_f\) | \(k_g\) | \(Cov\) | \(d_{ij}\) (nm) | \(f(Cov)\) | \(N/aggregate\) |
|-----------------|-----------------|-----------------|---------|---------|---------|-----------------|-----------|-----------------|
| 0%He - 30%Laser | 9.9             | 161             | 1.77    | 4.1     | 0.88    | 1.17            | 0.03      | 1041            |
| 20%He - 30%Laser| 6.8 & 11.3      | 127             | 1.71    | 4.83    | 0.90    | 0.67            | 0.03      | 748             |
| 40%He - 30%Laser| 5.6 & 15.2      | 99 & 159        | 1.79    | 3.86    | 0.88    | 0.7             | 0.03      | 864             |

3.4. Pyrolysis parameters study

The influence of two main pyrolysis parameters on the size distribution and physico-chemical characteristics of nanoparticles has been investigated, and results are exposed in Figure 12.

While the size of the primary nanoparticles (from 5 to 30 nm) and the 69 nm particles (from 30 to 100 nm) do not depend significantly of the experimental conditions, the median diameter of the aggregates is significantly smaller for 10 % of laser power than 30 %. Moreover, for a constant laser power, as the helium flow rate increases, the median diameter of aggregates strongly decreases. This significant evolution is mainly due to the helium dilution which mitigates the agglomeration of nanoparticles in the reaction zone.

Simple dilution in an inert gas induces several changes in the reaction. First, if the amount of reacting precursor molecules and total pressure are kept constant, the total gas flow is increased, decreasing the residence time in the laser zone and so decreasing the reaction duration and temperature. Second, if the global density is kept constant in the reaction zone, the dilution gas acts as a thermal bath. The collisions frequency between precursor-based dissociated species is reduced, as the reactant molecules partial pressure is decreased, which increases the cooling rate of the reaction by gas diffusion and quenches more rapidly the particles growth. With a high diffusion coefficient, helium appears to be an efficient dilution gas to quench the particles growth. The growth process is essentially driven by diffusion.
4. Conclusion

On-line measurements of particle size distribution at CEA/Saclay laser pyrolysis line have been achieved by employing various state-of-the-art as well as innovative measurement instrumentation and techniques. The correlation between various equivalent diameters is under development.

Three median diameter modes were identified. The first around 15-20 nm is attributed to primary particles, the second ranging from 150 to 350 nm is the aggregation/agglomeration mode, and the last one around 70 nm is still to be investigated but may be composed of silica oxide nanoparticles produced by the combustion of remaining silane. It is almost interesting to notice that nanoparticles are not strongly linked between each other and denote less than 14 % of overlapping while nanoparticles produced by combustion are strongly agglomerated [13]. Finally, the fractal dimensions observed for all the different operational point are closed to 1.80 and confirm that the aggregation/agglomeration processes are mainly governed by the diffusion.

Since these experimental campaigns are the first ones carried out on the IRAMIS/SPAM laser pyrolysis reactor, present results are promising and several issues need to be deeply investigated. The first one deals with the pyrolysis parameters study which may be further analyzed to understand the helium dilution and laser power effects on the overall production and aggregation/agglomeration of nanoparticles. The second key issue will be to verify the possible production of silica oxide by silane combustion in case of leak in the reactor. Finally, further investigations are needed on the monitoring of nanoparticles by such laser pyrolysis and on the way to retrieve the physic-chemical parameters of these particles in the most representative and continuous way.

Monitoring size of nanoparticles on production line in real time gave valuable information that could be used in a full automated synthesis set up, as a feedback for process parameters adjustment.

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