A CFX BASED MODEL FOR SI/C/N CERAMIC NANO-POWDER SYNTHESIS BY THE LASER PYROLYSIS

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ABSTRACT

A computational model was developed for the ceramic powder synthesis by the laser pyrolysis. The model took into account heat and mass transfers under experimental conditions. Simulations were performed by using the commercial Computational Fluid Dynamics (CFD) package CFX by adjusting or developing specific subroutines for the synthesis process.

NOMENCLATURE

α_{abs} absorption coefficient (m/N)
P total cell pressure (atm)
I_0 incident laser energy density (W/m^3)
ΔL absorption length (mm)
STP Standard Temperature and Pressure

INTRODUCTION

For manufacturing nanocomposite ceramics, the synthesis of nanosized powders, offers a promising way for structural applications, allowing higher temperature values than those allowed by metallic super alloys.

This synthesis was developed by CVD (Chemical Vapor Deposition), arc-plasma-heated or laser pyrolysis processes (Cannon et al 1982). The latter is the interaction between an infrared laser beam and a gas precursor or a liquid in aerosol form. The principle is based on the resonance phenomena between the emitted laser frequency (continuous CO_2, $\lambda=10.59$ μm) with at least one of the reactant absorption band. The powder obtained by this method shows very interesting characteristics, the small reaction volume and the ability to maintain steep temperature gradients allow the accurate control of the nucleation rate, permitting the formation of fine particles.

The control of these powders during their synthesis requires the understanding of coupled physical and chemical phenomena. Indeed, the nucleation and the growth of the particles depend directly on the resulting temperature, dynamic and species fields. These parameters are related to the operating conditions including conductive, convective and radiative heat transfers. In recent work (Amara et al 2002), the necessity of 3D extension is underlined by considering the 2D-axisymmetrical geometry, used by Akmandor (1985).

The present work focuses on the use of the three dimensional model of the reactor in order to characterize the influence of key parameters for the laser synthesis, namely the laser intensity and the cell pressure.

MODEL DESCRIPTION

Context of the study

Except for Akmandor's (1985) work at the beginning of the eighties, the majority of the published research focus on the development of the experimental part. Akmandor built a simplified model, incorporating the gas dynamics and the chemical reactions. The simulations were limited to a 2D-axisymmetrical geometry on a domain around the jet; the thermal heat transfer did not take into account the mixture between the carrier and the reactive gases. The latter is very important in the cooling process of the reactive gas. The actual experiment is three-dimensional and the powder synthesis may be influenced by some supposed minor phenomena taking place in the full reactor in the Akmandor (1985) calculations. Therefore, the facts that in experimental configuration, the laser radiation is in one dimension (exp. Y-Y axis) imply that, the problem is not axisymmetric. In our model, all thermal transfers (convection, conduction) are tacked into account.

In order to understand the solid particle formation mechanism and the relationship between experimental parameters (laser power, pressure, etc) and resulting powder characteristics, three-dimensional simulations are required.

Nowadays, powerful calculation are developed in such a way that complex geometries are taken into account, incorporating depth analyse of the physical phenomena. An industrial Computational Fluid Dynamic (CFD) package is used (CFX software); this software is based on finite volumes approximation, allowing the modelling of fluid flows in more or less complex geometry, and including reactive flow.

Geometry

A model was developed to represent the laser pyrolysis synthesis. Steady state solution of fluid flow is a required condition for a good reproducibility of the synthesis process and especially for the powder characteristics.

As a first step, the energy loss of the system by the particles thermal radiation is not taken into account. The

system incorporating the chemical species and the solid particles is under development.

The model consists of coupled conservation laws involving Navier-Stokes, energy and chemical species equations. The system of Partial Differential Equations (PDE) is formulated on primitive variables and solved on unstructured grid.

The investigated geometry (figure 1), is based on experimental configuration developed in our laboratory. It consists on the interaction between a silane jets surrounded by an annular argon flow (carrier gas) and an infrared laser radiation. The laser has a fixed diameter permitting the use of focused or unfocused rays.
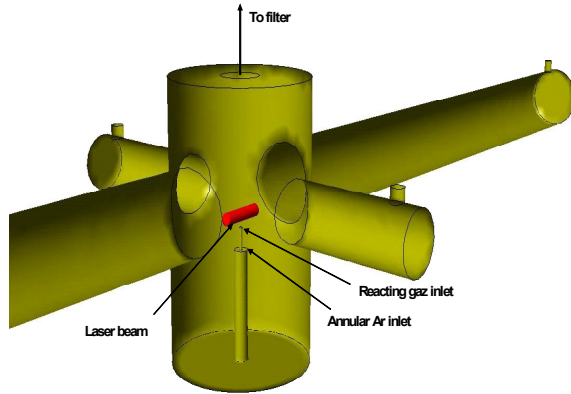

Figure 1: Geometry of the reactor.

Physical aspect

The present work deals with interaction between the laser radiation and the reactive gases. The majority of the sources yield their energy without any discrimination concerning the classically known molecular vibration states. For the laser pyrolysis of silane, the system uses a well defined quantity of energy. This energy is not sufficient for breaking down the molecular bonds. However, the vibrational states are changed.

A condition is necessary to increase the reaction rate to a significant level in which the excitation energy is in the same order of magnitude as the activation energy. Approximately, 30 photons are needed for the silane decomposition to produce *SiH3* and *H* (Ea ≈ 318 *kj/mol*, 3.3 *eV/molecule*). Several mechanisms (collisions, radiation) must be involved to reach this dissociation. From the macroscopic point of view, absorption of the laser radiation occurs according to Beer-Lambert law (Marra 1983):

$$I = I_0 \left[1 - \exp(-\alpha_{abs} P \Delta L) \right] \qquad (1)$$

The absorption coefficient depends on the temperature broadening effect, but its value is not tabulated; however an average value of *0.005 m/N* will be taken in this study (Akmandor, 1985).

The thermal decomposition reaction at *700 K* can be expressed as:

$$SiH_4(g) \xrightarrow{700K} Si(s) + 2H_2(g)$$
$$\Delta H = -30 Kj/mol \qquad (2)$$
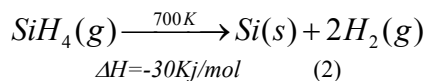
It was shown that this decomposition is a result of 120 intermediate steps (Coltrin et al 1984), which gives rise to many radicals such as *SiH2* or *C₂H₆*, but the global decomposition is limited by the reaction producing the silylene:

$$SiH_4(g) \rightarrow SiH_2(g) + H_2 \qquad (3)$$
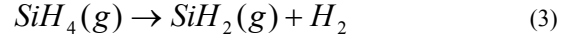
The rate of reaction 3 is given by (Coltrin et al 1984):

$$\frac{d[SiH_4]}{dt} = [SiH_4] \cdot 5 \times 10^{12} \exp\left(\frac{-52.2 Kcal/mol}{RT}\right) \qquad (4)$$

In the developed numerical model, only the initial reaction leading to the dominant component formation of silylene is taken into account. This assumption is justified by comparing characteristic time scales of the various involved phenomena: convective time scale based on a fluid characteristic distance (in our case the diameter of the laser beam) to the flow characteristic speed (inlet) giving $t_{convection} \approx 1s$. The reaction time scale is based on the rate of the reaction. For silylene decomposition, $t_{reaction} \approx 10^{-6}s$. It is noted that the reactive transfers are infinitely faster than the convective transfers.

RESULTS

To understand the effect of the process on the reaction, two key parameters for the laser synthesis are considered presently: the effect of the laser intensity and the pressure. Computational results are presented for a cell meshing of 36635 nodes carried out with refinement in the vicinity of the strong gradients areas as the laser source and the laser/gas interaction. Physical parameters are presented on the table 1.

Table 1: Physical parameters

Silane flow rate (cm³/min)	38
Argon flow rate (cm³/min)	1000
Silane nozzle diameter (mm)	1.2
Argon nozzle diameter (mm)	19.7

Effect of the laser intensity

Calculations show that the maximum temperature increases significantly with the laser intensity (figure 2). This has a consequence on the collected particle size. Indeed, the particle size is proportional to $T^{3/5}$ (Ring 1996). In experimental results, Marra (1983) observed that, an approximate tenfold increase in laser intensity resulted in only 7% increase in the particle diameter. Consequently, the maximum particle size achievable by the laser synthesis technique is limited.
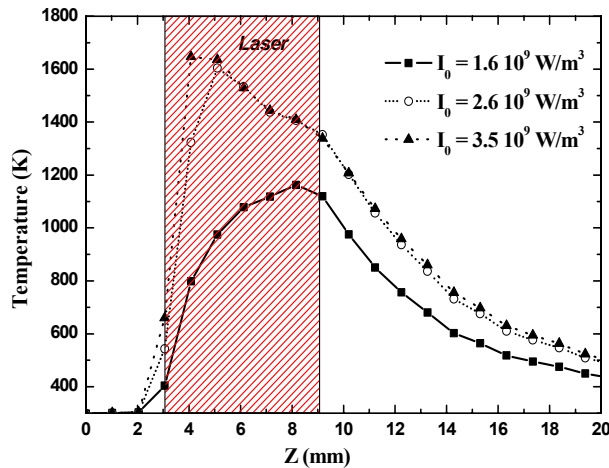
Figure 2: Maximum reaction temperature as a function of distance above the inlet nozzle (Z (mm)) for various laser intensity. (Total pressure =0.2 atm, silane flow rate 38 cc/min).

Effect of the pressure

An increase in total cell pressure, results on an increased peak temperature (figure 3). This indicates that, a slower velocity (the velocity is inversely proportional to the pressure) leads to a longer residence time within the laser beam.

Marra (1983), remarked that a pressure increase produces a larger particle diameter, but there is no effect on the conversion efficiency, particle chemistry, or agglomeration process.
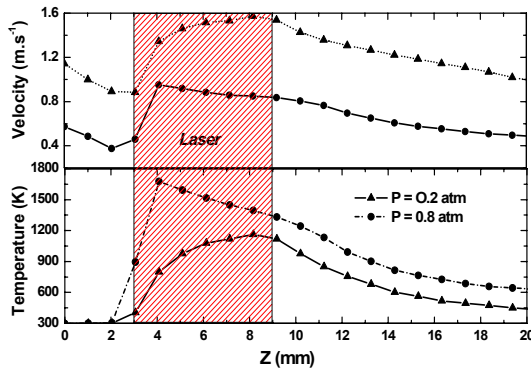

Figure 3: Maximum temperature variation and velocity, versus the distance above the inlet nozzle (silane flow rate 38 cm^3/min, I_0=1.6E 9 W/m^3).

Effect of the carrier gas flow rate

Two simulations were made to examine the effect of diluting the reactant gas stream with argon, this affects heating rate. Indeed, the overall absorption coefficient is decreased, because argon does not absorb IR radiation at 10.6 μm. Figure 4 shows that the heating decrease and that the reaction was more confined, as the flow rate of argon increase. Therefore, we note in comparison between figure top and down (figure 4) that increasing the argon flow rate confines the reaction zone.
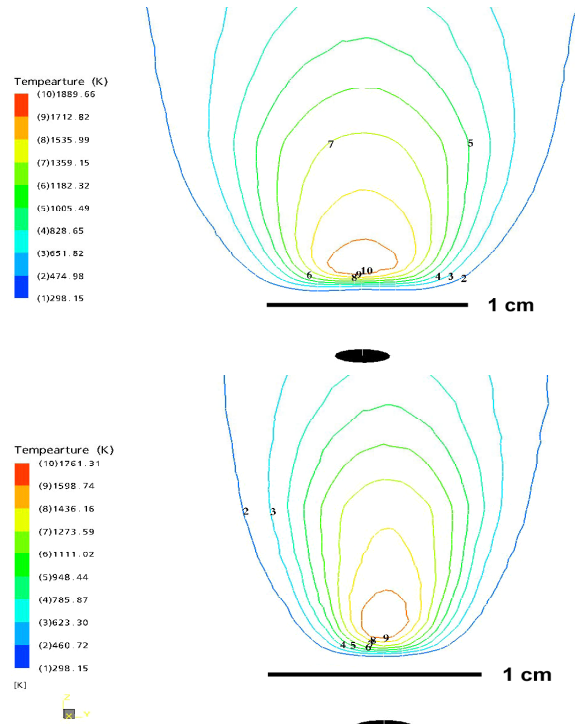

Figure 4: Map of temperature for two flow rates of dilute gas. Top : 500 cm^3/min (STP); down: 1000 cm^3/min (STP).

Flame stability

Under certain conditions, Akamdor (1985) mentioned occuring oscillation of the flame. The flickering of the flame has a direct consequence on the nucleation and on the particles growth. Indeed, chemical processes occur within the flame.

The present model, confirm a presence of this phenomenon. Figure 5 (top), represents variation of temperature in two positions above the inlet nozzle (Z= 6 mm top left and Z=10 mm top right). The agreement between our calculations and the experimental points (Akmandor 1985) fit well.

Several mechanisms can cause instability for the reaction zone, notably important parameters like the cell pressure, the silane flow speed, and the reactor geometry. The first and second parameters are co-dependent, because of the fact that the velocity is inversely proportional to the pressure.
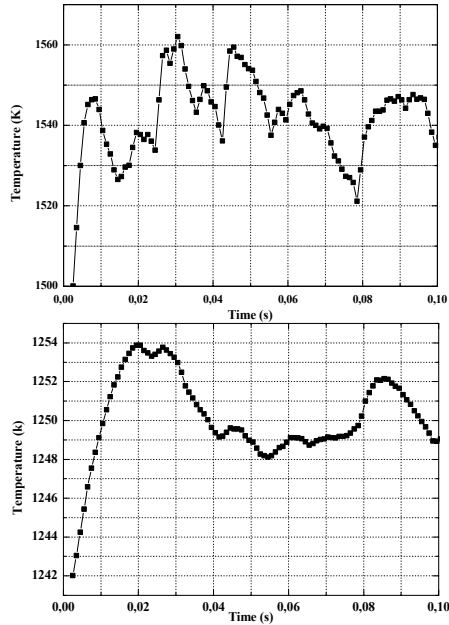
Figure 5: Temperature variation versus time at different locations (P=0.6 atm, SiH_4 38 cc/min STP, I_0= 1.6E9W/m^3). Tensient simulation.

Possible reasons of flame oscillation due to the velocity of the silane is explained by the fact that, when the flame speed is greater than the silane flow speed, the flame front propagates towards the unreacted silane volume, consuming the unburned gas at a rate faster than the supply rate (Akmandor, 1985). The time between two consecutive "*flame-outs*" will define oscillation rate. For the purpose of our calculation, the flame speed has been estimated as 0.77 m/s. In condition corresponding to *P=0.6 atm, SiH$_4$ 38 cc/min STP, I$_0$= 1.6E9W/m^3* (figure 5), the velocity is equal to *0.6 m/s*. This suggests that silane velocity affects the instability. Another factor which disturbs the flame is the presence of a recirculation zone or vortex. All calculations predict a presence of this region (figure 6).
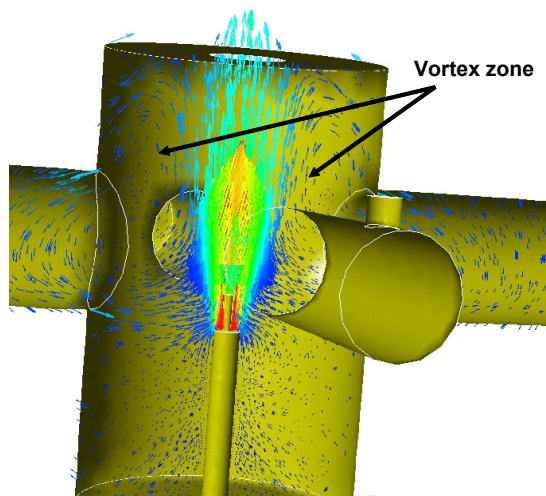

Figure 6: Velocity field inside the reactor, showing the presence of a recirculation zone.

The presence of a large-scale frequency oscillations (figure 5), indicate that, the cause of flame flickering was

not unique. We note different factors which can disturb flame: Reactor geometry, Natural frequency and Kelvin-Helmholtz instability.

We not previously, that a presence of vortex can cause flame oscillations. For stabilised flow, we consider two geometry configurations, in which the diameter of the outlet was doubled, this can reduce gas accumulation in the exit of reactor.

We note (figure 7), that recirculation zone are reduced in second configuration, and the vortex structure are vanished. This result show the importance of outlet diameter, the bigger is the exist powder, the smaller is the recirculation zone, the more probable is the stability of flow. This study can not take into account collecting of powder. Indeed, excessive powder accumulation in the collecting filter, can causing backpressure waves to travel up stream in the cell and disturb the reaction zone (Akmandor, 1985). This indicates the advantage of a bigger powder collector.

Another source responsible of oscillations is the Kelvin-Helmholtz instabilities at interface between the high-velocity and low velocity fluids (Ellzey et al, 1990), indicating that typically frequencies are a few hundred Hertz, our results are in agreements (figure 5).
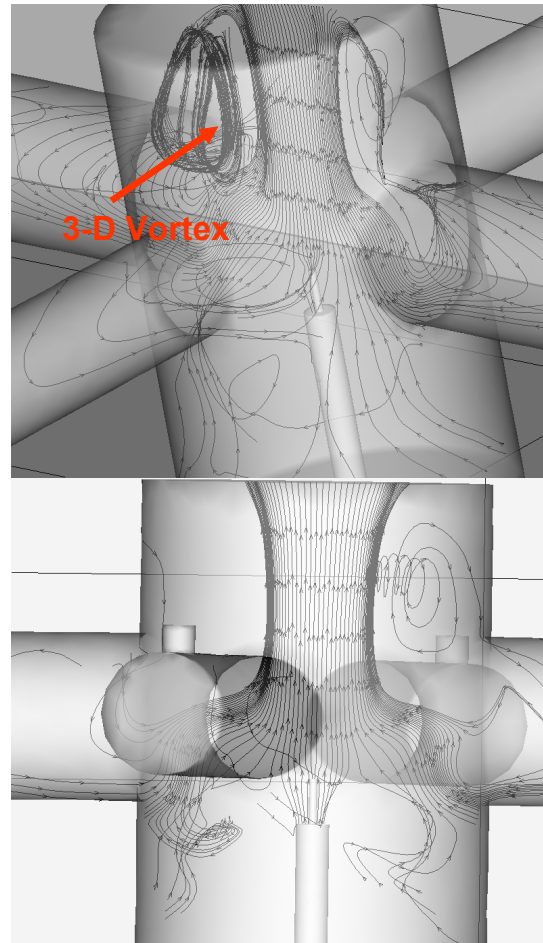

Figure 7: Comparison of two reactor configurations. Up configuration outlet diameter *20 mm*. down configuration outlet diameter *40 mm*.

CONCLUSION

A computational model for the laser synthesis is developed. The temperature, dynamic, and chemical species field are computed. These calculations are carried out in three dimensions, and take into account all thermal transfers. These results correspond to an extension of those of Akmandor's limited to a two-dimensional axisymmetric geometry, and are in agreement with experimental data.

Present calculations highlight the presence of flickering flame predicted by experiments; the two major parameters affecting reaction zone instability are the pressure and the reactor geometry.

This work clarifies the behaviour modelling of the several reagent gas mixtures *(SiH4, CH4, NH3 ...)* in the laser beam, in order to optimise the synthesis conditions of *SiCN* powders.

REFERENCES

AMARA M., HOURLIER D., EL GANAOUI M., GOURSAT P. Modélisation numérique de la synthèse de poudres nanométriques Si/C/N par pyrolyse laser, *J. Physical & Chemical News*, in press, 2003.

AKMANDOR I. S., (1985). *Theoretical and Computational Models of Reacting Silane Gas Flows: laser Driven Pyrolysis of Subsonic and Supersonic Jets. PhD thesis of Cambridge*, MIT.

ELLZEY J. L., ORAN E. S., (1990), Effects of Heat release and gravity on an unsteady diffusion flame, *Twenty-Third Symposium (International) on Combustion, the Combustion Institute,* 1635-1640.

MARRA, RA (1983). *Homogenous nucleation and growth of silicon powder from laser heated gas phase reaction*. PhD thesis of Cambridge, MIT.

MICHEL E. COLTRIN RJM, JAMES A. MLLERR., (1884). A Mathematical Model of the Coupled Fluid Mechanics and Chemical Kinetics in a Chemical Vapor Deposition Reactor. *J. Electrochem Soc*. **131**, 425-434.

RING, TA (1996). *Fundamentals of Ceramic Powder Processing and Synthesis*. Acadeemic Press, 255-306.

SUHAS V. PATANKAR, AND SPALDING, D. B. (1970). *Heat and Mass Transfer in Boundary Layers*. 2nd Edition, Intertext Books, London.

W. R. CANNON SCD, J. S. HAGGERTY, R. A. MARRA., (1992). Sinterible Ceramic Powders from Laser-Driven Reactions: I, Powder Characteristics and Process Variables. *J. American Ceram. Soc*. 65 (7):324.

W. R. CANNON SCD, J. H. FLINT, J. S. HAGGERTY, R. A. MARRA., (1982), Sinterible Ceramic Powders From Laser-Driven Reactions: II, Process Description and modeling. *J. American Ceram. Soc*, 65 (7):330.

CFX5 user manual developed by AEA technology, http://www.software.aeat.com/.