ABLATION IN CARBON/CARBON COMPOSITES: MICROSCOPIC OBSERVATIONS AND 3D NUMERICAL SIMULATION OF SURFACE ROUGHNESS EVOLUTION

J. Lachaud[1], G. L. Vignoles[1], J.-M. Goyhénèche[1], J.-F. Epherre[1,2]

[1]Laboratoire des Composites ThermoStructuraux (LCTS),
UMR 5801: CNRS-SAFRAN-CEA-UB1,
Domaine Universitaire de Bordeaux – 3, Allée de La Boétie, 33600 Pessac, France

[2]Commissariat à l'Energie Atomique (CEA), CESTA, BP2, 33114 Le Barp, France

ABSTRACT

The design of efficient thermal protection systems relies on the use of *ablative* thermostructural materials with controlled surface recession, such as Carbon/Carbon (C/C) composites. Hence the coupled physical phenomena leading to carbon loss and resulting in a global surface recession have to be known. Here, the focus is set on a multi-scale three-dimensional study of appearing composite surface roughness which, directly or not, induces a strong enhancement of heat and mass transfer and consequently increases ablation velocity.

First, surface roughness of C/C samples submitted to arc-jet ground test (quite representative of real conditions) is mainly investigated by scanning electron microscopy (SEM). A description, a classification and an analysis of multi-scale surface roughness features are proposed.

Then a three-dimensional reaction-diffusion local model is set up to explain the formation of the typical needle shape of the carbon fibers in emerging yarns. A 3D numerical code using Brownian motion simulation technique (gas diffusion) and random sticking events (heterogeneous reaction) has been implemented to solve a diffusion-reaction model. The surface is described with a simplified Marching Cubes approach, which allows to handle efficiently its alteration by ablation. The simulation method is shown to give, in a reasonable computing time, results in correct agreement with SEM observations.

Moreover, such an approach could contribute to the identification of material or flow intrinsic properties through morphological analysis of the roughness features.

INTRODUCTION

Spatial vehicles often encounter severe environments during atmospheric crossing. Since the speed can reach many km/s in dense atmosphere, the flow close to the nosetip can be hypersonic. In this case a thin bow shock surrounds an inviscid flow (eulerian flow), while a dynamic boundary layer develops in the vicinity of the wall[1] (see left part of Fig. 1). Typically, temperature of the flow may reach $7000\,K$ and it may lead to a maximal wall temperature of $4500\,K$ for pressures higher than $100\,bar$.[2] For such an environment, the design of thermal protection systems relies on Carbon/Carbon (C/C) composites, which possess the best compromise between thermal, thermo-chemical and mechanical properties.[3] However, a high interfacial mass transfer, strongly coupled with boundary layer transfer phenomena, leads to surface recession. Indeed, C/C composites are progressively destroyed by oxidation, sublimation and, up to a certain extent, mechanical erosion. These physico-chemical phenomena, denoted by the term *ablation*, are globally endothermic. Hence they reduce the wall

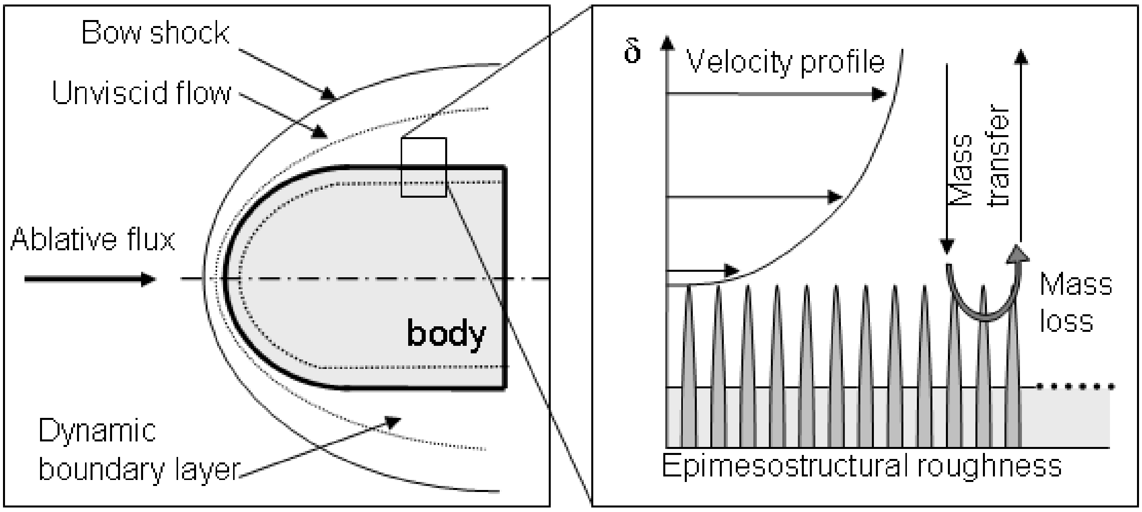


Figure 1: Hypersonic flow over a blunt body at macroscopic (left) and yarn (right) scales.

temperature and the heat flux that penetrates the internal structure.

Ablation of C/C composites quickly leads to surface roughness. Roughness induces an enhancement of heat and mass transfer which puts up ablation velocity via two major phenomena: (i) it increases the chemically active surface of the wall; (ii) it contributes to the laminar-to-turbulent transition in the dynamic boundary layer. If general phenomenological tendencies are predictable, the understanding of the interaction between the flow and the material has to be improved. In this work, an effort is done to improve this understanding in laminar flow conditions through the observation, the study and the modelling of roughness evolution. This document includes four parts:

1. First, a description and a classification of multi-scale surface roughness features appearing on C/C composites are proposed;

2. Then, a three-dimensional reaction-diffusion local model is set up to explain the formation of the typical needle shape of emerging carbon fibers;

3. A homemade 3D numerical simulation code, called AMA, developed to solve moving interface problem coupled to "heterogeneous reaction/ mass transfer" processes is succinctly presented;

4. Last, the model established in part 2 is solved using AMA. Results, which are in correct agreement with observations, enable optimistic outlooks for the improvement of ablation understanding, and the determination of material intrinsic properties.

ROUGHNESS DESCRIPTION AND CLASSIFICATION

Test and observation conditions

Unfortunately, it is quite difficult to recover samples from real flight experiments. As far as roughness is concerned, arc-jet tests are supposed to be representative of real flight

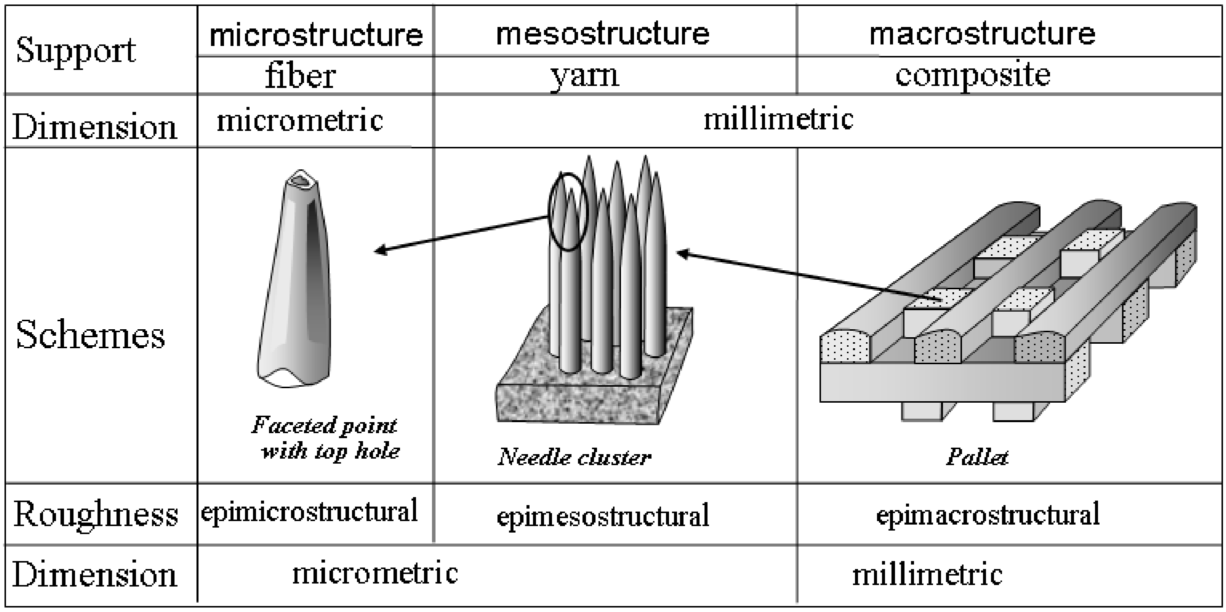


Figure 2: Multi-scale roughness on a 3D C/C ablated material : synthesis tabular.

conditions. This study is restricted to arc-jet tests; however its results may have some interest for real flight ablation simulation.

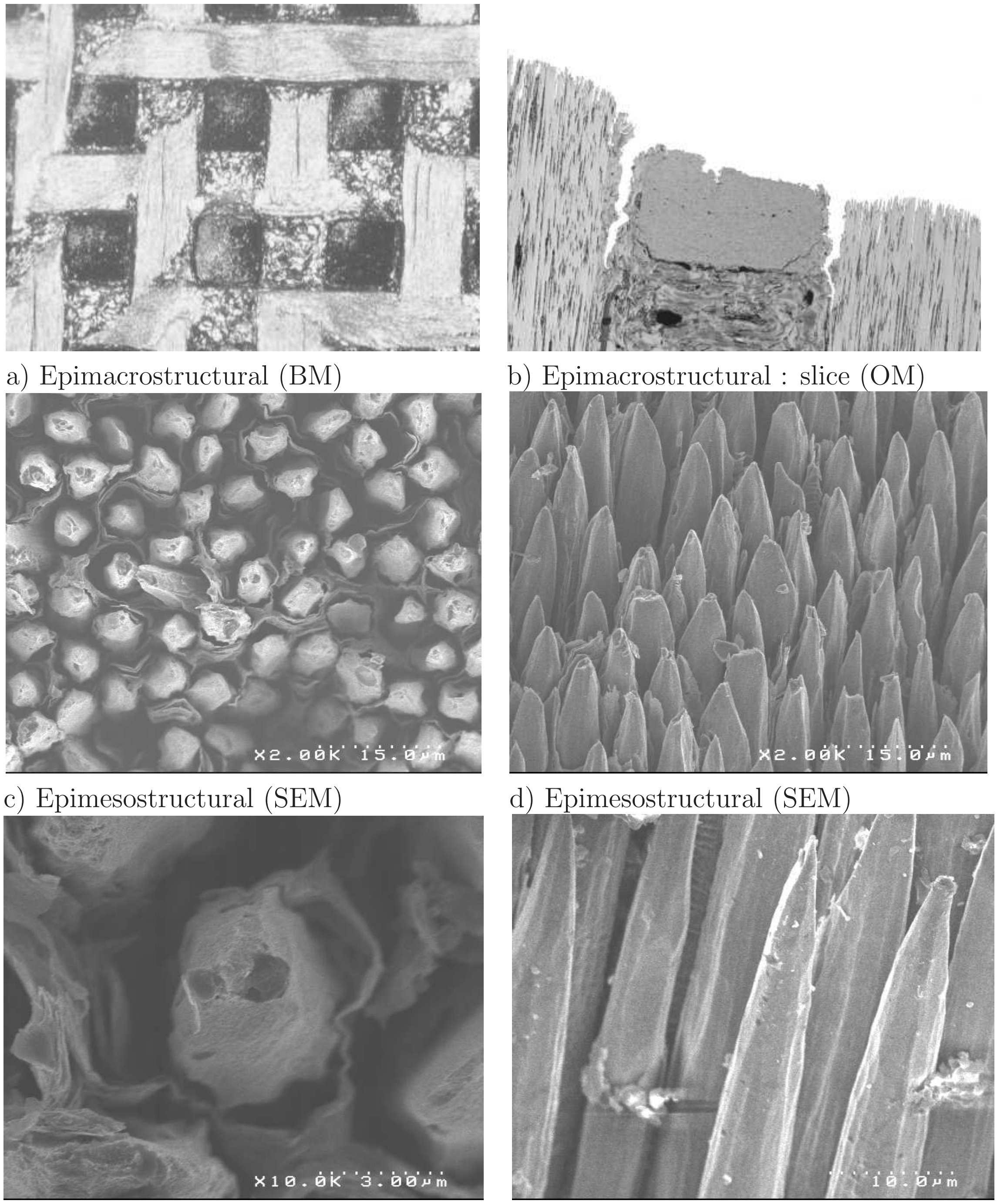
C/C composite samples, made from a 3D ex-PAN carbon fiber woven preform and a pitch-based carbon matrix, has been submitted to arc-jet ground tests in stagnation point configuration. The material temperature was high enough ($3000\,K$) to enable both oxidation and sublimation. However, the efficient 3D C/C structure prevents the sample from being notably eroded during ablation. Surface roughness has been observed by binocular magnifier (BM), optical microscope (OM) and scanning electron microscopy (SEM).

Description and classification

As shown on the left sketch of the Fig. 2, 3D C/C is an heterogeneous multi-scale material, on which roughness features can appear during ablation. The small points represent the fiber sections (microstructure). Several thousands of fibers are linked together into yarn with a pitch-based matrix (mesostructure). Then, yarns are orthogonally fit together into a pattern repeated by translation on a cubic lattice. This macro-structure leads to a network of parallelepipedic macro-pores (located near each node of the lattice), which are partially filled with pitch matrix.

A classification of the observed roughness features according to their length scales is presented on Fig. 2. For each scale, a sketch and a name are given:

1. Epimacrostructural roughness takes place on the lattice. It seems to result from the difference of reactivity between yarns and extra-yarn pitch-based matrix. Mechanical erosion sporadically occurs through the detachment of an extra-yarn matrix octet. The section of emerging yarns (tangent or perpendicular to surface) is slightly undulating. Indeed, if edges of initially square section of yarns are emerging, creating crenels, they



a) Epimacrostructural (BM)
b) Epimacrostructural : slice (OM)
c) Epimesostructural (SEM)
d) Epimesostructural (SEM)
e) Epimicrostructural (SEM)
f) Epimicrostructural (SEM)

Figure 3: Micrographies of 3D C/C surface roughness after ablation.

are smoothed out to a wavy form by ablation. A BM photograph of the surface and a OM micrograph of a polished slice, presented on Fig. 3-a and b, associated to the knowledge of the material structure, enable us to sketch the "pallet" scheme.

2. Epimesostructural roughness develops at the end of emerging yarns, and looks like "needle clusters" (resp. "needle layers") for yarns perpendicular (resp. parallel) to material surface. In the literature, many micrographs show such roughness features on carbon-based composites during ablation by oxidation[4,5] or both oxidation and sublimation.[6–8] As shown on photographs 3-c and d, due to an important recession of the intra-yarn matrix, fibers, which are less reactive, are partially stripped, become thinner, and acquire a needle shape.

3. Epimicrostructural roughness appears on the microstructure. Fiber tips are faceted (Fig. 3-f). Moreover, Fig. 3-c and e also shows holes on the top of the fibers.

According to the classification presented above, ablation phenomena exhibits the material structure through roughness set-up. Geometrical features mainly follow the material structure. Then, let us call it structural roughness to make a difference with a purely physical roughness which has already been observed on homogeneous material and modelled.[2] This physical roughness consists in scalloped morphologies and is not correlated to material structure. The cause seems to be a dynamical effect based on the concurrence between mass transfer and chemical reactions.

Regarding structural roughness, physical phenomena are also underlying (reactivity differences and possibly perturbations of local mass transfer). As a result, models including structure and physics has to be taken in consideration.

MODEL SET-UP

Position of the study

In the literature, the global phenomenology of ablation at macroscopic scale is widely described from the fluid point of view, i.e. the material is considered as a reactive and thermally conductive homogeneous interface).[1,9–15] However, as the scope of this study is to understand structural roughness set-up, the problem is approached here from the composite material point of view. Moreover the choice is made to focus on the mesostructure scale ("needle clusters") and to study the stationary profiles.

Phenomenology

The global phenomenology has roughly been described in the introduction of this document. Let us now complete it with the yarn scale specific phenomenology. It is linked to macroscopic scale on Fig. 1. As far as reactivity is considered, the C/C composite yarns are heterogeneous. Indeed, for both oxidation (Eq. 1) and sublimation (Eq. 2),

$$C_{(s)} + O_2 \rightleftharpoons CO_2 \tag{1}$$

$$n\,C_{(s)} \rightleftharpoons C_n \tag{2}$$

the reaction rates of fibers (more organized turbostratic carbon[3,16]) are lower than the matrix ones. Mass loss is strongly coupled to mass transfer perpendicularly to the wall.[2] In

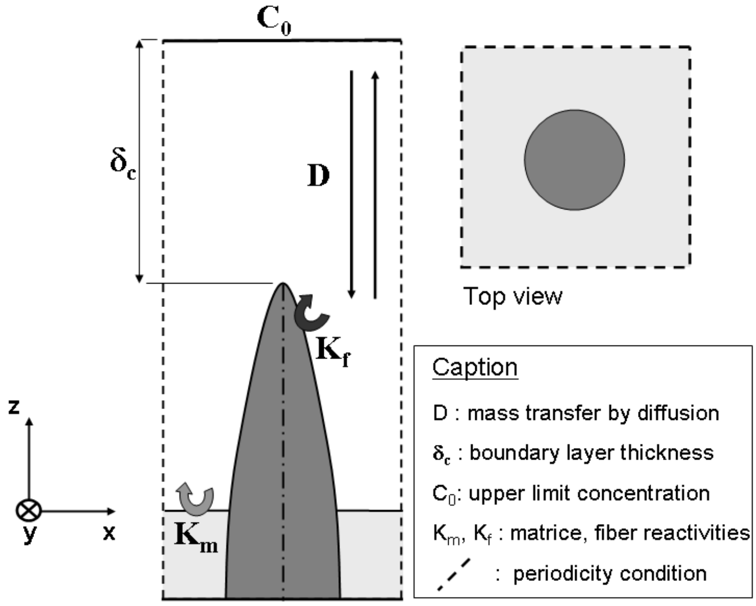


Figure 4: Scheme of the elementary pattern and of the proposed model

laminar flow conditions, mass transfer is mainly diffusive and can be described by a boundary layer formalism. Laminar boundary layer thickness (δ) has been estimated by Navier-Stokes equations resolution, its value is of the order of one millimeter. For each species i, it is reasonable to deduce mass concentration boundary layer thickness (δ_{c_i}) from δ by the following relation:[17]

$$\frac{\delta}{\delta_{c_i}} \approx Sc^{\frac{1}{3}} \tag{3}$$

where $Sc = \nu / D_{iM}$ is the Schmidt number (with ν and D_{iM} ($m^2 s^{-1}$) resp. kinematic viscosity and binary mass diffusion coefficient of species i in the gas mixture M), close to unity in gases.

The difference of reactivity between fibers and matrix leads to a local difference of ablation velocity which turns into surface roughness, unless gas diffusion phenomena brings a limit (see part 4).

Composite surface model and conditions

The proposed model is sketched on Fig. 4. On this scheme the stationary roughness is represented; however at initial time, the fluid/solid interface is flat. This profile has therefore to be obtained using a moving interface modelling.

The model includes the following hypotheses:

- Material:
  - The yarn is made of fibers and matrix;
  - Matrix and fibers are assumed homogeneous and isotropic;

– The composite is supposed to be only ablated by a first order oxidation reaction* (represented by Eq. 1); that is to say temperature is rather close to 3000K than higher;

– Yarn section is supposed infinite in transverse directions;

- Physical phenomena:

  – Mass transfer is restricted to binary diffusion of the single reactant (O_2) in nitrogen (diffusion of the gaseous by products (CO_2) is neglected);

  – Chemical reaction is restricted to the surface;

  – Close to the wall, advection is negligible;

  – Thermal gradients are neglected ;

  – Stefan flux (due to mass transfer into the fluid) is neglected.

Let us write mass conservation of the reactant (of molar concentration C) in the fluid phase:

$$\frac{\partial C}{\partial t} + \nabla \cdot (-D \nabla C) \,=\, 0 \tag{4}$$

Relative boundary conditions are:

- On boundary layer top: $C \,=\, C_0$;

- At the fluid/solid interface : $(-D\nabla C) \cdot \mathbf{n} \;=\; -k_i C$ (where $\mathbf{n}$ is the normal to the surface, and k_i (m/s) the reaction kinetic constant of matrix $(i = m)$ or fibers $(i = f)$);

- Periodicity on the lateral boundaries.

The interface position ($z \,=\, h(x, y, t)$) is given by the coupled resolution of : $\frac{\partial h}{\partial t} \;=\; -v_s k_i C \mathbf{n}$ (where v_s is the solid molar volume). Moreover, δ_c is a constant, as the top of the boundary limit moves together with the wall.

DIRECT NUMERICAL SIMULATION IMPLEMENTATION AND VALIDATION

Numerical implementation

To solve this problem in 3-D and in non-stationary regime, a numerical simulation code, named AMA, has been developed on a Monte-Carlo random-walk principle. As sketched on Fig. 5, AMA, which is a C ANSI implementation, falls into five main parts:

- A 3-D image containing several phases (fluid/solids) is described by discrete cubic voxels method;

- The moving fluid/solid interface is determined by a simplified marching cube approach;[18]

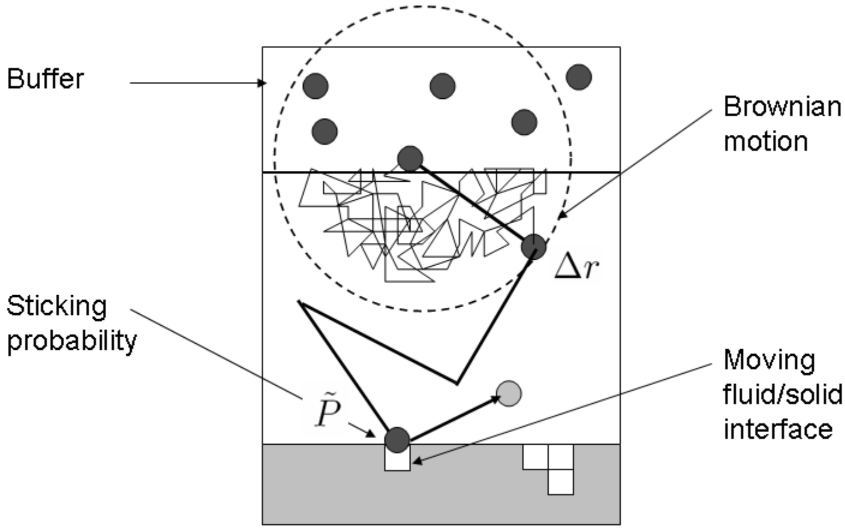


Figure 5: Scheme of the numerical simulation code AMA principle.

- Mass transfer by diffusion is simulated by a Brownian motion simulation technique,[19] which is a continuum (grid-free) and fast convergence method for diffusion in a continuous fluid. The time increment (Δt) is proportional to the square of space increment (Δr) and to the inverse of the binary diffusion coefficient (D).[20]

- Heterogeneous first order reaction on the wall is simulated by a sticking probability ($\tilde{P}$) adapted to the Brownian motion simulation technique.[21] The relation 5 has been deduced by a theoretical analysis. The value of α (which is close to 0.8) is obtained by a numerical study.

$$\tilde{P} = \frac{1}{1 + \frac{3/2\alpha D}{k\Delta r}} \tag{5}$$

- A Dirichlet upper boundary condition is simulated using a buffer.

AMA validation

AMA has been successfully compared to the 1-D (with i restricted to m) steady state diffusion/first-order reaction model reduced from the model proposed above. By solving equation 4, one obtains the analytical reactant flux at the interface (Φ):

$$\Phi = \frac{D}{\delta_c} C_0 \frac{1}{1 + \frac{1}{Da}} \tag{6}$$

where $Da = k_m \delta_c / D$ is a Damköhler number.

Fig. 6 illustrates the comparison between numerical simulation and analytical expression of Φ (cf. Eq. 6) when k_m varies. The maximal relative error is lower than 2.5%, whatever the values chosen for δ_c, C_0 and D.

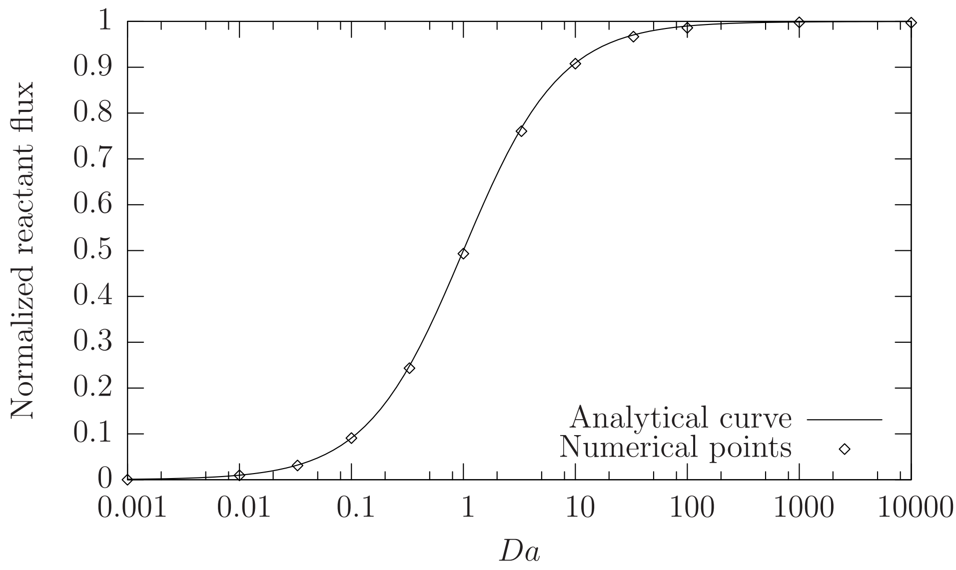


Figure 6: AMA validation by comparison to a 1-D model

NUMERICAL SIMULATION RESULTS

The lack of experimental data on turbostratic carbon reactivity to oxygen at high temperatures prevent us from doing a single and accurate simulation case. Moreover, the variety of turbostratic carbons is very large : reactivity may span as much as 3 orders of magnitude.[16] Consequently, it is more appropriate to perform a parametric study, using the model sketched on Fig. 4. The results are presented on Fig. 7. The influence of three dimensionless groups on the stationary roughness profiles of "needle clusters" is studied:

- Damköhler number for the fiber : $Da_f = k_f \delta_c / D$ (only k_f varies) (minimal value (min.): 0 , maximal value (max.): ∞);
- Reactivity ratio : $\tilde{k} = k_m / k_f$ (min.: 1 , max.: ∞);
- Fiber/cell ratio : $\tilde{r}_f = d_f / l$ (min.: 0 , max.: 1), with d_f: fiber diameter, and l: square base cell size.

The model sensitivity to each-one of these three dimensionless groups is tested from a central case ($Da_f = 0.1$, $\tilde{k} = 10$, $\tilde{r}_f = 0.6$).

For each simulation case, the steady state regime is reached after a computing time ranges from 1 to 24 hours with a Xenon CPU 3.2GHz processor.

Let us describe the morphological evolutions of roughness features as the dimensionless groups are varying. Peak-to-valley roughness increases together with:

- Fiber/cell ratio ($\tilde{r}_f$) in an almost homothetic way;
- The inverse of Damköhler number (Da_f) from a flat to an almost pyramidal geometry;
- Reactivity ratio ($\tilde{k}$) from a flat to a needle-like geometry.

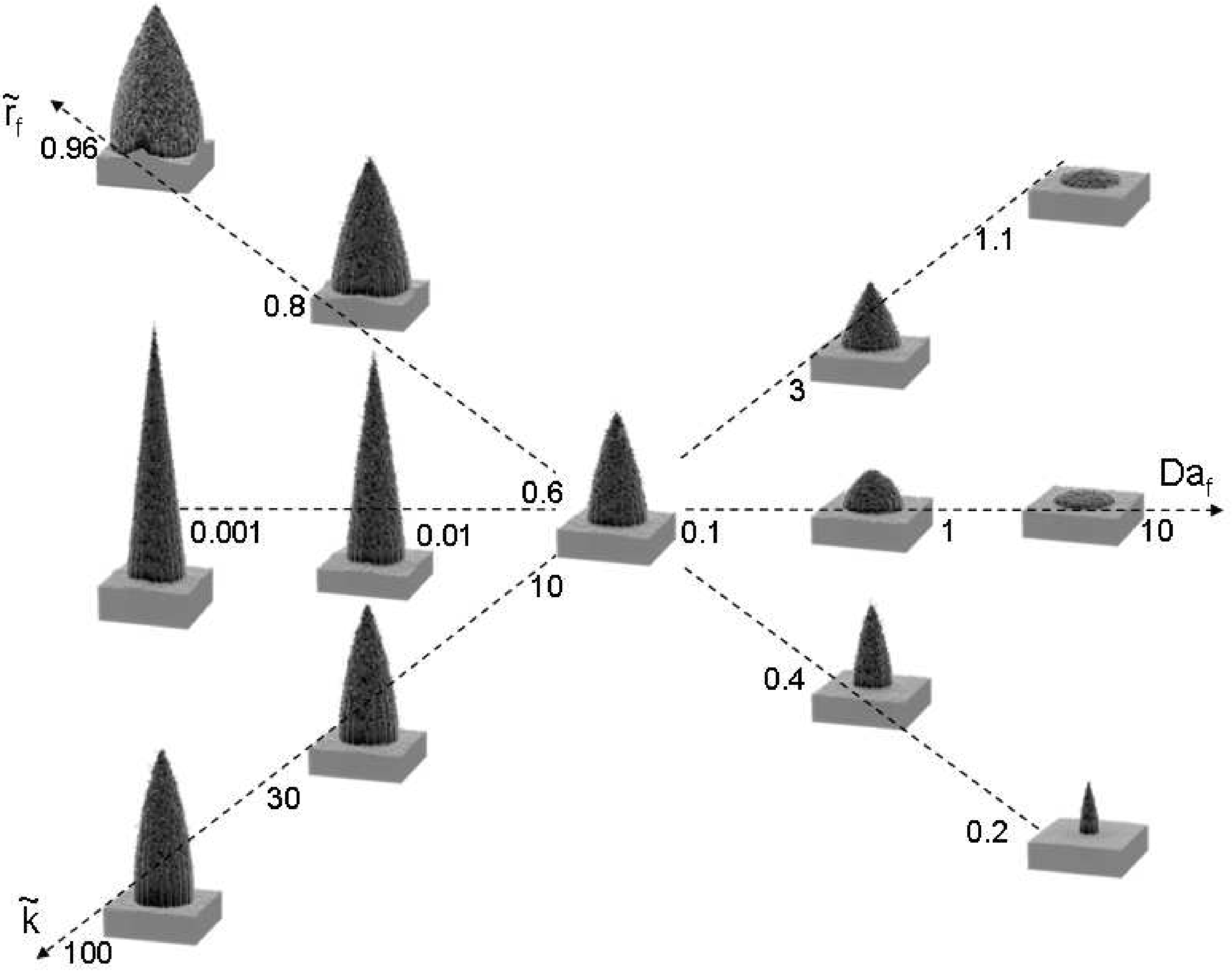


Figure 7: Parametrical study at mesoscopic scale

Limiting cases are observed. On the right side of the Fig. 7, roughness set-up becomes impossible, since the problem turns out to be 1-D for at least one of these reasons (from top to bottom): (i) homogeneous solid ($\tilde{k} \rightarrow 1$); (ii) diffusive limitation ($Da \rightarrow \infty$); (iii) homogeneous solid ($\tilde{r}_f \rightarrow 0$). On the left side, the peak-to-valley roughness is maximal since (from top to bottom): (i) fiber diameter is maximal ($\tilde{r}_f \rightarrow 1$), (ii) reactive limitation on fiber and matrix is reached ($Da_f \rightarrow 0$), (iii) diffusive limitation on matrix is reached ($\tilde{k} \rightarrow \infty$).

As a result, it is possible to analyze real morphologies through those first results. Of course, the simplicity of the model used has to be kept in mind. A comparison of Fig. 7 to micrographs of Fig. 3-d and f tends to show that the actual material reactivity ratio between fiber and matrix is high. Moreover, as fibers tips seem more rounded on micrograph 3-d, fibers are unlikely to be in reactive limitation. Nothing can be said on the matrix behavior.

It is reasonable to conclude that this simple results can qualitatively explain the development of "needle clusters" roughness features and contributes to understand ablation.

CONCLUSION AND OUTLOOK

In this work, the origin and development of roughness on a 3D-C/C ablative composite during atmospheric crossing are tackled. First, using as reference arc-jet test samples, multi-scale roughness is observed, classified and briefly analyzed as a whole. Then the focus is set on well-know "needle clusters" roughness features which develop on perpendicularly emerging yarns. A simple heterogeneous reaction/diffusion model is proposed. The use of an efficient homemade 3D numerical simulation code (validated by comparison to a 1-D analytical model) enabled to perform a parametrical study. Despite the lack of experimental data for 3D validation, results are promising, since the proposed model can qualitatively explain roughness development. Moreover, it is likely to give pertinent information on reactive regime conditions and helps us to improve the understanding of the role of coupled physicochemical phenomena in ablation.

Up to a certain extent, this study opens the possibility to determine, by inverse analysis, either mass transfer properties or material intrinsic reactivities.

FOOTNOTE

*Sublimation modelling is quite similar and gives the same stationary profiles since dimensionless groups values are equal.

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