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Oxidation behavior of nozzle throat carbon/carbon composites featuring variable densities

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Abstract

Nozzle throat C/C composites, densified by CVI process, display a non-homogenous in-depth density, leading to unpredictable surface recession rates. Thermogravimetric analysis and 3D-image correlation were used to understand the behavior of C/C composites of various density at 1273K during half an hour under dry air. An increase of the material lifespan with matrix volume fraction (i.e. mass density) was observed. However, C/C oxidation behavior dependency with architectural and environmental parameters was still not obvious. Thus, an analytical modeling has been developped to help understand and predict C/C behavior under oxidizing atmospheres, which also constitutes a handy tool to help designing porous C/C composites.

Nomenclature

Latin symbols		Greek symbols	
A	*Reactivity contrast*	ε	*Porosity*
C	*Molar concentration* ($mol.m^{-3}$)	δ	*Affected length (m)*
D_0	*Binary diffusion coefficient* ($m^2.s^{-1}$)	Ω_s	*Solid molar volume* ($m^3.mol^{-1}$)
D_p	*Effective diffusion coefficient* ($m^2.s^{-1}$)	ϕ	*Solid volume fraction*
k_{het}	*Heterogeneous reactivity* ($m.s^{-1}$)	ρ	*Density* ($g.cm^{-3}$)
$\mathcal{L}$	*Characteristic length (m)*	σ_v	*Effective surface area* (m^2)
m	*mass (g)*		
S	*Surface* (m^2)	Subscripts and superscripts	
Sh	*Sherwood number*	a	*Relative to overall material*
t	*Time (s)*	b	*Relative to the surface gas-solid boundary*
		c	*Relative to the composite*
Abbreviation		eff	*Relative to an effective surface*
μ-*CT* X-ray Computed Tomography		f	*Relative to the fibers*
TGA Thermogravimetric Analysis		m	*Relative to the matrix*
TPS Thermal Protection System		0	*Relative to initial state*

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1. Introduction

Carbon/carbon (C/C) composites are known for their high thermo-mechanical resistance properties in various domains. They are used as Tokamak armors, aeroplane brake disks, thermal protective systems for atmospheric re-entry vehicles, solid and liquid rocket motor nozzle throats and divergents.[11,22,24] Physico-chemical conditions can be harsh in these types of application (high pressure and gas velocity, very high temperatures, oxidizing atmospheres, solid particules attacks). However, carbon is known to be weak under oxidizing atmospheres. It may start degrading under dioxygen from 400°C at atmospheric pressure due to active oxidation and/or sublimation.[7,23] Because of this and of mechanical erosion, C/C materials experience surface recession. Besides, nozzle throat C/C composites considered in this study are densified with a Chemical Vapor Infiltration (CVI) process which is known to lead to multi-scale porosity and density gradients in parts.[11] This is an additional constraint because recession rate, which strongly depends on density, is thus non-linear in-depth.

Predicting material recessions under specified conditions is essential, especially in aerospatial applications. In the past two decades, carbon materials ablation behavior by chemical etching has been experimentally studied and modelled under various conditions. Lachaud et al.[16] considered a ideal fully dense 3D C/C composite oxidized in a cylindrical reactor at 898K under dry air at atmospheric pressure. They developped a modeling strategy to predict material behavior from that of its components (i.e. fibers and matrix). They set up two dimensionless parameters, a reactivity contrast number and a Sherwood number translating the reaction/diffusion competition. The non-additive property of fibers and matrix intrinsic kinetics was proved, whereas it was only a guesswork until then.[5,20,26] Ferguson et al.[9] applied the same modeling strategy to a carbon-fully infused resin composite by a numerical method.
On the other hand, the ablation of porous TPS (Thermal Protection System) materials has also been studied. Lachaud et al.[17] initiated an elementary model for the oxidation of carbon fibers bundles in order to identify fibers kinetics, from TGA (Thermogravimetric Analysis) oxidation results under dry air atmospheric pressure at 873K. The Thiele number, which is commonly used to describe the efficiency of porous catalysts, has been reformulated to fit the reaction-to-diffusion competition in the porous bulk of carbon fibrous materials. Panerai et al.[21] reoperated the method on carbon fibrous preforms in an air-flow tube under various temperatures and oxygen partial pressures to assess reaction-to-diffusion regimes in atmospheric re-entry, via the Thiele modulus. Later, Ferguson et al.[9,10] reconsidered the preliminary strategy with the help of X-ray micro-tomography images and a computational framework, assuming oxygen containing atmosphere. Vignoles et al.[25] went further considering simultaneous nitridation and nitrogen recombination in carbon fibrous preforms in a nitrogen plasma atmosphere, developing simultaneously an analytical model and image-based numerical simulations.
As a matter of fact, the above-mentioned studies have highlighted the roles of phases reactivity contrasts and surface/volume reaction-to-diffusion ratios. However, as the models developed so far are two-phase models (either fibers/matrix or fibers/pores), they are not suitable for C/C materials featuring an initial porosity.

Actually, due to their CVI densification process, porous C/C composites are three-phase materials (fibers/matrix/pores) and former efforts to model C/C behavior under oxidation are not sufficient in that case. There is a genuine need to improve knowledge in porous C/C behavior under oxidizing environment, and more specifically the interplay of gas diffusion and surface chemical reactions of two phases with differing reactivities. In that goal, this work is focusing on experimental tests with variable initial densities, which are actually missing in litterature, and on the identification of the key parameters allowing the most suitable description of their behavior.

2. Experimental study

The behavior of C/C composites under various oxidizing atmospheres has been widely studied in the past decades.[3,15,17] The carbonaceous composite materials considered in these studies are exclusievly highly densified C/C composites (porosity lower than 20%). Some works emerged considering the evolution of the effective or specific surface area with oxidation.[12–14] However, data concerning the behavior under oxidative atmospheres of C/C with different initial porosity and effective surfaces areas are missing. This is the reason why the present study started with an experimental study on the oxidation of C/C samples featuring various levels of initial porosity (i.e. matrix volume fraction).

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2.1 Materials and methods

C/C composite materials of the present study are made of an ex-PAN 3D needle-punched reinforcement architecture which has been carbonized.[18,19] Fibers texture is then densified by CVI process with a Rough Laminar Pyrocarbon (RL PyC) matrix with various processing times to obtain samples of different matrix volume fractions (i.e. densities). The samples are cubic-like with a 6mm-width.

A thermogravimetric apparatus (TGA) with a precision balance measuring mass loss at any time have been used for oxidation tests. They have been carried out at 1273K under a dry air atmosphere (mixture of 20% of O_2 and 80% N_2) with an airflow of 2L/h at atmospheric pressure.

Burn-off rates, defined as $\frac{\Delta m}{m_0}$ (%), and recession rate, set as $\frac{1}{S_{eff}\rho_c}\frac{dm}{dt}$ (m.s^{-1}) were computed, where m_0 is the initial mass sample, m the mass sample during test, S_{eff} the geometrical sample surface and ρ_c the composite mass density. Then, the after test samples were characterized with an innovative method coupling micro-tomography (µ-CT) imaging and Digital Volume Correlation (DVC). A synthetic schematic of the method is given by Fig. 1.

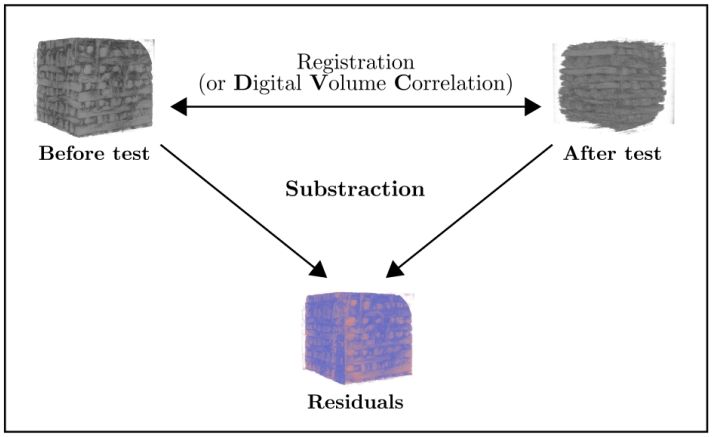
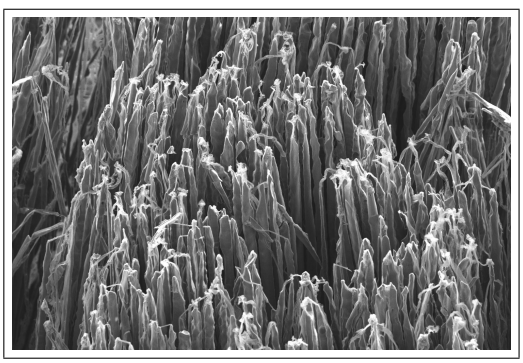
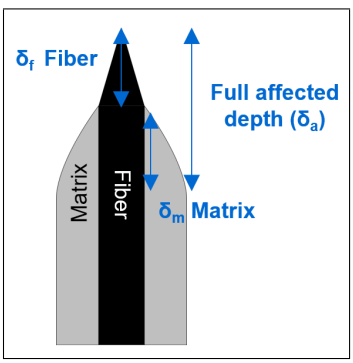


Figure 1: Schematic of the Digital Volume Correlation method

Before and after tests µ-CT images of the sample were acquired in a X-ray Computerized Tomography apparatus and registered in order to be substracted voxel by voxel. The residuals (or differences between both images) are equivalent to oxidized material which has disappeared. The final morphology of the samples is shown Fig. 2 (a). Matrix, fibers and overall affected lengths can now be defined on Fig. 2 (b) and are identified on post-tests µ-CT images and residuals imaging. The normalized length parameter ξ_i is defined as $\xi_i = \frac{\delta_f}{\delta_a}$.



(a) Post-oxidation C/C surface SEM image



(b) Schematic of after test alterations

Figure 2: Post-mortem SEM image and affected lengths schematic

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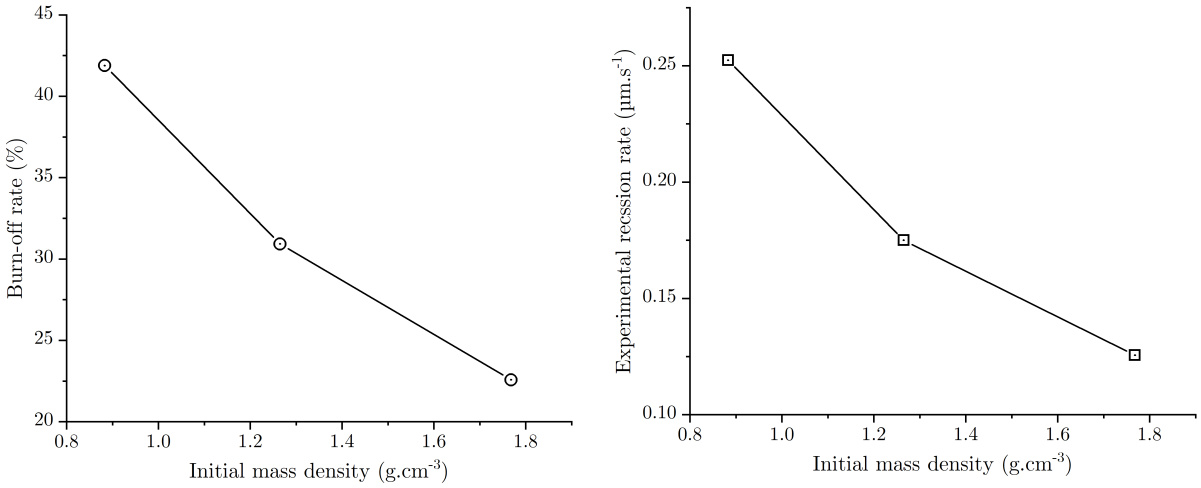
2.2 Results

Burn-off and recession rates, as defined in section 2.1, are displayed in Figs. 3a and respectively 3b. The denser the material is, the longer it lasts and the less its surface recedes. Thus, the lifespan of the material increases with its mass density (i.e. matrix volume fraction).



(a) Burn-off rate at 1273K

(b) Experimental recession rate at 1273K

Figure 3: Experimental results of burn-off and recession rates after half an hour of oxidation at 1273K

Fig. 4 illustrates the different affected lengths of the material with initial mass density. The same conclusion is given : the denser is the material, the less it is affected in depth and the more fibers are protected by the matrix. However, these experimental observations are not enough to understand the overall material behavior dependency with its environment and with the different architectural parameters.

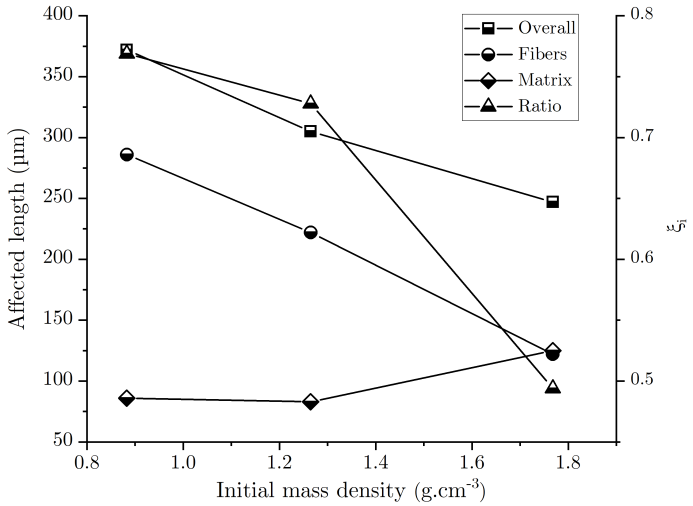


Figure 4: Characterization results of affected lengths after oxidation after half an hour of oxidation at 1273K

2.3 Numerical reconstruction

The oxygen concentration at the sample surface is not trivial to assess as important surface and volume diffusion effects occur. A numerical reconstruction of the oxidation test is required, based on experimental results. It has been performed on CFD software *ANSYS Fluent 17.2* with a geometry and a mesh adapted to the apparatus used for this study. The works of Lachaud et al.[17] and Zancanaro et al.[28] were a starting point for this macroscopic reconstruction.

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3. Interpretation of the experimental results

3.1 1D analytical modeling

The experimental study of porous C/C under oxidizing conditions brings a trend about their behavior with density. However, it is not enough to grasp parameters dependency. Hence, an analytical model has been developped considering the coupling between architectural features and environmental conditions. It relies on the solution of gas and solids mass balances in fibers and matrix domains respectively, given by Eqs. 1 and 2 respectively. The methodology is quite similar to the ones described by Lachaud et al.[16] and Vignoles et al.[25] excepting that a third phase has to be included here (either pores or matrix), and mass balances are solved in each domain individually. Details of the resolution are provided in a forthcoming paper.

$$\frac{\partial C(x,t)}{\partial t} + \nabla \cdot \Big(- D_p \varepsilon(x,t) \nabla C(x,t) \Big) = -\sigma_v(\phi_i(x,t)) k_{het,i} C(x,t) \; i \in \{f;m\} \tag{1}$$

$$-\frac{\partial \phi_i(x,t)}{\partial t} = \Omega_{s,i} \sigma_{v,i}(\phi_i(x,t)) k_{het,i} C(x,t) \; i \in \{f;m\} \tag{2}$$

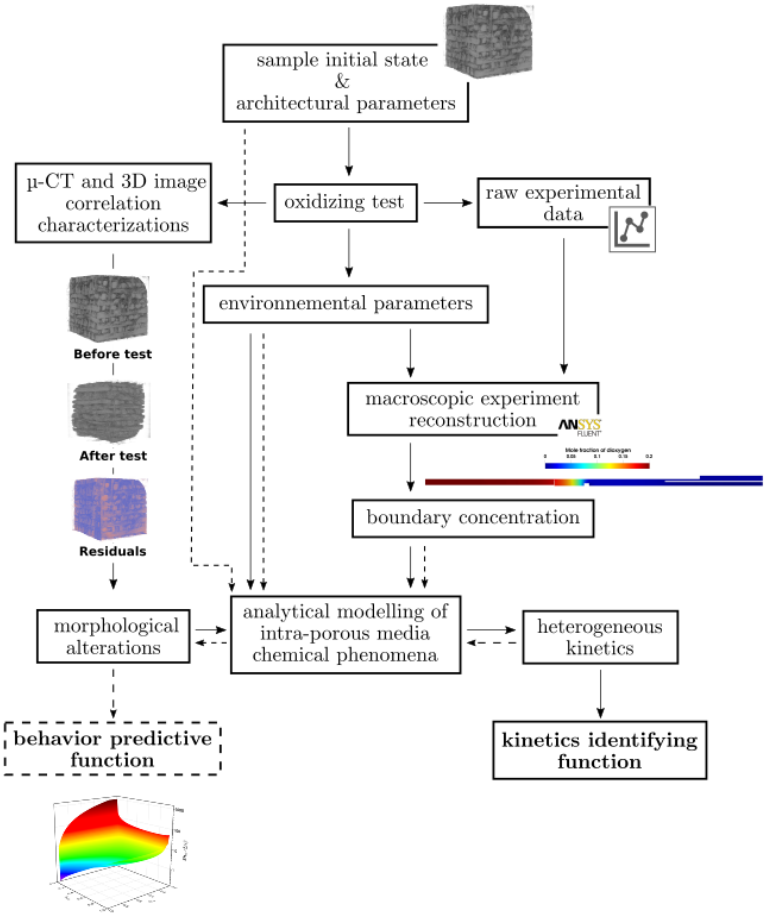

Figure 5: Analytical, numerical and experimental global approach

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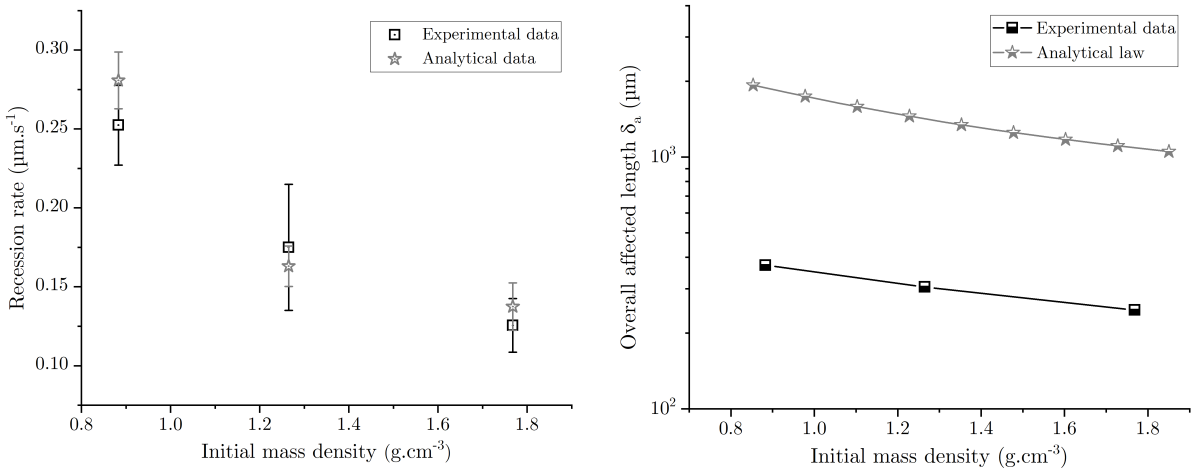
Fig. 5 gives an overview of the global approach articulated around the analytical model. It can be operated in two different ways. The solid line path on Fig. 5 shows that starting from experimental results and numerical reconstruction of the test, fibers and matrix kinetics can be determined. Thus, the model is used as an indentifier of heterogenous kinetics. On the other hand, the dotted line path shows that knowing fibers and matrix heterogenous kinetics, C/C behavior can be predicted in any oxidizing atmosphere, in terms of affected lengths, recession rate and effective surface reactivity.

3.2 Comparison to experimental results

In order to assess and validate the model, recession rates from experimental tests are compared to analytical results computed from morphological alterations data and reconstruction of the environment (Fig. 6a). Experimental recession rates and analytical results agree very satisfactorily with each other, within their respective confidence margins. Having a critical look at these data, it is recognized that the recession rate depends principally on the boundary concentration computed with the numerical reconstruction. At 1273K and for that system, the boundary oxygen concentration is close to 0.16 mol.m^{-3}. Its accuracy is ensured from 10 to 20% and is more likely to be lower than higher. Thus, a fluctuation of the boundary concentration of that percentage feeds through recession rate and became even more consistent with experimental data.



(a) Recession rate experimental / analytical

(b) Affected length experimental / analytical

Figure 6: Comparison of analytical recession rate and affected length values to experimental data

On an other hand, the evolution of the experimental overall affected length with density compared to the law given by the analytical procedure are given in Fig. 6b. Even if the results can differ from a factor 4 to 5, the tendencies are consistent. The discrepencies between experimental and analytical values might come from the choice made for the matrix and fibers characteristic lengths. They can be optimized in the future. However, one can notice that the analytical model overrates real post-mortem alterations, wich provides a satisfactory margin when it is used as a predicition model.

3.3 Comparison to literature data

In a perspective of validation, fibers and matrix heterogenous kinetics indentified with the analytical modelling are compared to data from litterature. As kinetics for PyC matrix oxidation are scarce, even non existent, data from ex-pitch matrix and resin-derived carbons have been collected for comparison.[1,4,6] Carbonaceous materials derived from the pyrolysis of pitches or resins are known to be less resistant to oxidation than PyC materials because of a lower degree of graphitic organization. For PyC matrix, a higher activation energy and a pre-exponential factor are then expected. Thus, Fig. 7 indicates a satisfying consistency between litterature and analytical data in terms of kinetics as well as activation energy. Regarding fibers kinetics, data in literature for ex-PAN fibers oxidized in air are abondant.[2,6,27,29] A good adequation is found as well between fibers data from literature and analytical modeling on Fig. 7 except for the ex-PAN fibers used by Tong et al.[27] which display a lower cristallite size than the fibers used for the present study. This means a lower resistance to oxidation and thus a lower activation energy, as oxidation behavior is closely linked to defects density.[8,20]

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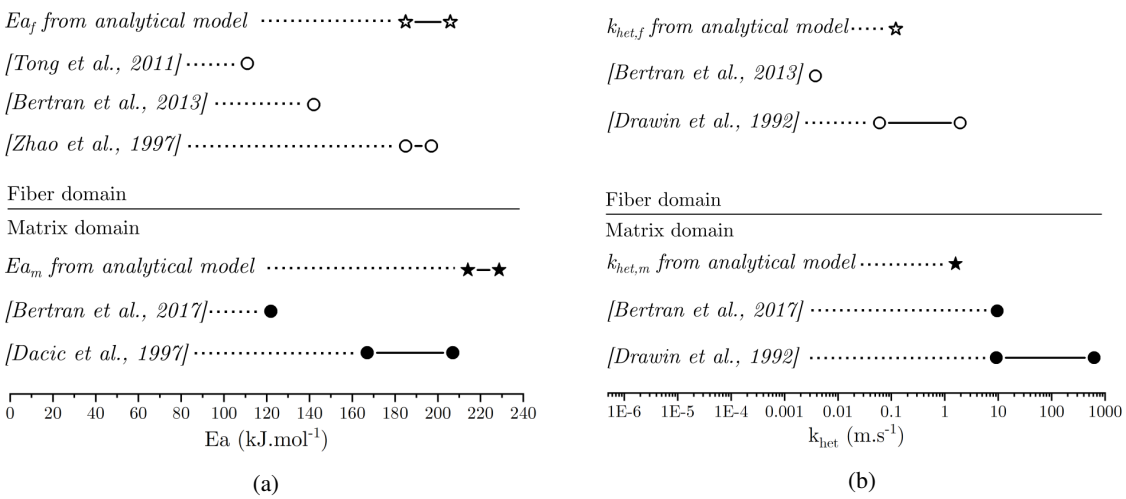

Figure 7: Comparison of analytical results at 1273K with litterature

4. Discussion

The utlimate purpose of this model is to assist in the designing of porous C/C materials. The analytical model pays attention to the Sherwood number $Sh_i (i \in \{f;m\})$ and the reactivity contrast A which are dimensionless parameters, initially defined by Lachaud et al.,[16] and satisfying the following equations :

$$Sh_i = \frac{k_{het,i}\mathcal{L}_i}{D_0} \; i \in \{f;m\} \tag{3}$$

$$A = \frac{k_{het,m}}{k_{het,f}} \frac{\Omega_{s,m}}{\Omega_{s,f}} \tag{4}$$

Sh_i, which depends on environmental conditions with the presence of $k_{het,i}$ and D_0, measures the competition between diffusion and reaction over a characteristic length $\mathcal{L}_i$. On an other hand, A is the ratio of fibers and matrix heterogenous reactivies and evaluates the leading phase in the oxidation behavior. Figs. 8 and 9 display the evolution of $\frac{Sh_f\lambda_f^2}{9\omega}$ and $\frac{Sh_m\lambda_m^2}{4}$ (λ_i being length ratios equal to $\frac{\delta_a}{\mathcal{L}_i}$), with fibers and matrix volume fractions for different values of A. Knowing the oxidizing environnement, either for fibers or matrix, Fig. 8 or 9 may help determining the best $\{\phi_{f,0};\phi_{m,0}\}$ combination that will achieve the lowest overall material affectation length δ_a.

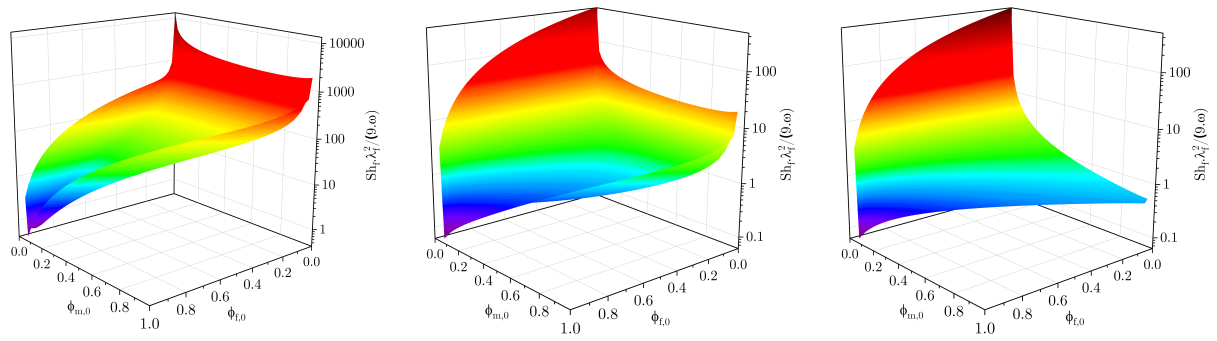

Figure 8: Operating graphs of the affected length δ_a with environnemental conditions depending on fibers behavior (Sh_f) and architectural parameters ($\phi_{f,0}$, $\phi_{m,0}$)

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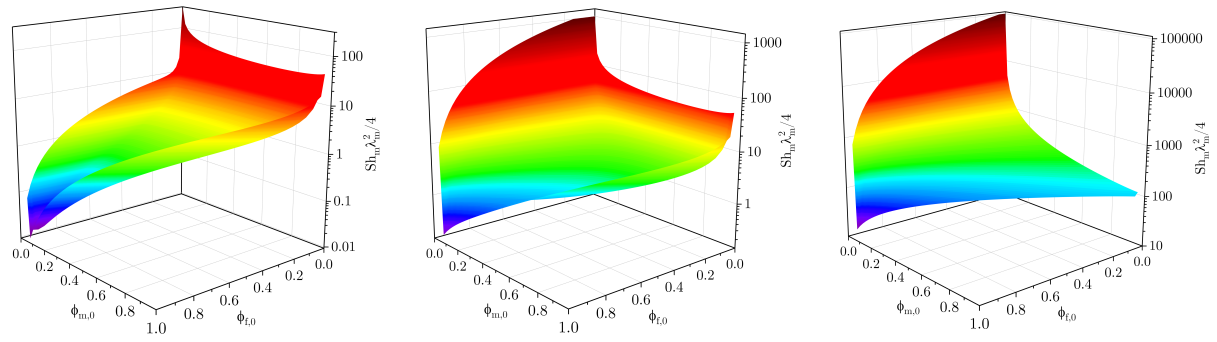

(a) A ≪ 1 (b) A = 1 (c) A ≫ 1

Figure 9: Operating graphs of the affected length δ_a with environnemental conditions depending on matrix behavior ($S\,h_m$) and architectural parameters ($\phi_{f,0}$, $\phi_{m,0}$)

5. Conclusion and Perspectives

By means of an experimental study in a TGA apparatus, the understanding of porous C/C behavior under oxidizing environment have enriched existing literature, especially concerning the impact of initial porosity. Complementary data on surface evolution (effective and specific surfaces, pore sizes distribution) with oxidation are upcoming.

The development of a three-phase analytical model completes existing models of fully densified C/C and carbon fibrous materials, with excellent agreement with experimental results. After experimental and bibliographic verifications, the whole approach is validated and can help designing C/C for any application in an oxidizing environment that might display the same architecture with a small or large amount of pores.

Besides, the identification of an heterogeneous reactivity value at 1273K for the PyC matrix is completely brand new as data on the oxidation of PyC material are scarce. Thanks to experiments carried out at different high temperatures (not detailed here) and by the use of the analytical model, we also identified an activation energy for this type of matrix.

This model still needs to be improved and adapted to other types of porous C/C featuring different architectures. On the other hand, we are looking to identifying heterogeneous kinetics for fibers and especially for PyC matrix under CO_2 and H_2O corrosion.

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