MULTI-SCALE MODEL OF PYROCARBON CHEMICAL VAPOR INFILTRATION FROM PROPANE: QUANTITATIVE VALIDATION ON KINETICS AND NANOTEXTURE

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Introduction

Chemical Vapor Infiltration (CVI) [1] is a technique of choice for the preparation of the pyrocarbon matrix of high-performance Carbon/Carbon composites [2] with applications in very highly demanding conditions, like atmospheric reentry heat shield parts [3], rocket nozzles [4], high-performance aircraft brakes [4], or Tokamak plasma-facing components [5]. More recently, it has been shown that CVI of pyrocarbon was equally useful for the reinforcement of open-cell carbon foams [6] for vibration damping [7] and shock absorption uses at high temperatures [8]. In this process, the preform (a fiber arrangement or the unconsolidated foam) is to be coated by a matrix obtained through the cracking of a hydrocarbon precursor gas. The thermal decomposition of the precursor gas yields complex mixtures of radical and molecular species. Their eventual reaction with the preform leads to the formation of a pyrocarbon matrix. Its nanotexture and the overall deposit homogeneity deeply rely on processing parameters such as the gas composition, pressure, temperature, the residence time or the reactor surface/volume ratio [9-13]. In their turn, final composite thermo-mechanical properties and graphitizability are directly impacted by these characteristics [14]. A purely experimental optimization of CVI is very expensive and has motivated the development of numerical modeling of CVI.

Previous studies in this field have given extensive knowledge of precursor gas decomposition [15], the evolution of geometrical characteristics [16] and CVI of pyrocarbon was equally useful for the reinforcement of open-cell carbon foams [6]. Thermally cracked hydrocarbons are capable of acquiring accurate 3D images of the material structure. Our infiltration model makes use of high and low-resolution images to compute effective properties at different levels of preform description. This tool works on 3D representations, as those one can get by X-ray CMT, but it can also handle computer-generated images of idealized materials.

Experimental

The studied preforms were vitreous carbon foams with 60pni pore size and carbon fiber arrangements featuring a “2.5D” architecture (needled stackings of woven plies). All samples were cylindrical with 10mm in diameter and height. Their porosity, determined by the Archimedes method, was equal to 98% for the foams and 82% for the fiber arrangements. The experimental setup consists in a low-pressure hot wall tubular CVD reactor [24]. The tube diameter was 34 mm and the hot zone size (defined with a 10K precision) is 30 mm. The precursor gas was propane. Residence time, pressure and temperatures are listed in Table 1. In the experiment references, letter “P” refers to fibrous preforms and letter “F” refers to foams.

Table 1. Experimental conditions and deposition rates.

<table>
<thead>
<tr>
<th>Expt #</th>
<th>T (K)</th>
<th>Press. (kPa)</th>
<th>Res. time (s)</th>
<th>Time (s)</th>
<th>Dep. rate (μg.cm⁻².min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5-1</td>
<td>1323</td>
<td>5.0</td>
<td>0.1</td>
<td>28h30m</td>
<td>2.1</td>
</tr>
<tr>
<td>P5-2</td>
<td>1323</td>
<td>5.0</td>
<td>0.35</td>
<td>18h</td>
<td>1.7</td>
</tr>
<tr>
<td>P5-3</td>
<td>1323</td>
<td>5.0</td>
<td>3.0</td>
<td>15h</td>
<td>1.4</td>
</tr>
<tr>
<td>P2-3</td>
<td>1323</td>
<td>2.0</td>
<td>3.0</td>
<td>14h30m</td>
<td>3.8</td>
</tr>
<tr>
<td>P0.5-1</td>
<td>1323</td>
<td>0.5</td>
<td>0.065</td>
<td>22h</td>
<td>0.9</td>
</tr>
<tr>
<td>F1</td>
<td>1223</td>
<td>5.0</td>
<td>0.2</td>
<td>19h</td>
<td>4.9</td>
</tr>
<tr>
<td>F2</td>
<td>1223</td>
<td>5.0</td>
<td>3.0</td>
<td>11h55m</td>
<td>22.3</td>
</tr>
</tbody>
</table>

The deposit thickness distribution was measured by optical microscopy. The identification of the nanotexture of each infiltrated sample was accomplished by polarized Raman microscopy [25]. Deposition of three distinct laminar pyrocarbon nanotextures was performed. Their formation is linked to the process temperature and the residence time. When increased, one successively obtains rough laminar (RL), smooth laminar (SL) and regenerative laminar (RL) carbon matrix.

The approach has also been fed by CVD data, i.e. deposition rates on plain, non-porous substrates, performed in similar conditions in the same apparatus [24]. The infiltration model for the fibrous preforms makes use of 3D images at microscopic and macroscopic description.
levels. Indeed, previous studies have shown that the fiber arrangements studied here exhibit a bi-modal pore structure: one at the fiber scale and a second at the tow scale [26]. Both are accessible to X-ray computerized tomography but not with the same emission source. Detailed scans featuring distinct fiber bundles are only possible by using a synchrotron facility. Therefore the microscopic scale images of the fibrous preform were acquired at ESRF ID19 beamline in phase contrast mode. The effective pixel size was 0.7 \textmu m and reconstruction of the radiographs was performed by filtered back-projection [27]. A specific segmentation treatment [28] was used to separate the fibers for the porosity. Macroscopic scale acquisitions of the fibrous preform have been monitored by a lab-scale X-ray CMT apparatus (Phoenix X-ray Nanotome) at 25\textmu m per pixel resolution (after reconstruction). Foams have only been scanned with the latter setup, at 5\textmu m per pixel, since they do not display bimodal pore structure.

**Modeling**

The modeling strategy is decomposed into four steps as shown in Figure 1. Construction of the final reactor scale tool requires the outputs produced by the first three numerical models. Firstly, it must feature a semi-detailed mechanism for propane pyrolysis [11]. There are 41 species (from C1: CH\textsubscript{4}, CH\textsubscript{2}, etc... to C10: C\textsubscript{10}H\textsubscript{8}) and 133 reactions in this mechanism. In order to perform subsequent CVI computations, the reaction scheme is simplified, with a few lumped species and apparent reactions [29,30], as illustrated in Figure 2.

![Fig. 1 Scheme of the global modeling strategy.](image)

Using the CANTERA software [31], the applied pressure and temperature are imposed to the gas phase and species concentrations are computed as a function of time. The gas-phase maturation phenomenon is evidenced: the initial decomposition of propane gives first-generation species, most in C1 (methyl radical) and C2 (ethane, ethene); later on, acetylene and benzene appear; finally, higher molecular-weight species such as naphthalene occur. Homogeneous reaction rates are identified by the combination of this data and of the simplified scheme expressions.

![Fig. 2 Simplified (lumped kinetic scheme for the deposition of pyrocarbons from propane.](image)

The incomplete kinetic model is then introduced into the FLUENT computational fluid dynamics (CFD) solver and a mass, heat and momentum analysis in a 2D axi-symmetrical reactor is performed. The heterogeneous reaction rates are fitted by comparing numerically obtained deposition rates, for every set of operating conditions, with results from CVD experiments. When doing so favorably, concentration profiles of each species at the boundaries of the porous medium are also collected.

The complete kinetic scheme may then be introduced in the final preform-scale 2D axi-symmetrical mass balance FE solver for preform consolidation, which is based on FlexPDE software [32]. Gas transport may rely on viscous flow, ordinary (binary) diffusion, and rarefied gas flow (Knudsen diffusion) [33]. In the present case, since the gases may freely flow around the porous sample, no appreciable pressure buildup appears: consequently, viscous flow is rather negligible with respect to the other transport modalities, as usual in isothermal CVI.

Prior to simulation, the effective diffusivities and the internal surface area, given as functions of the pore volume fraction, have to be determined. In this goal, the 3D CMT images and the image-based infiltration models have been used. Deposit growth has been simulated in the high-resolution scans by using DMC, a homemade Monte Carlo Random Walk (MCRW) algorithm dedicated to fiber scale computations [22]. With this same tool, blocks representing different infiltration stages have been processed for the determination of the internal surface area and of the effective binary and Knudsen diffusivities [17,22,26]. The determined laws were then inserted into LIRWa, another homemade MCRW software suited to infiltration at the composite scale [23]. The resulting macroscopic scale laws are then inserted into the final reactor scale solver.

**Results and discussion**
Numerical simulations were performed following the described methodology for each preform and for the same experimental parameters. Table 2 proves that, whatever the physic-chemical conditions, agreement between experimental and numerical results is obtained.

The predominant nanotexture in each area is defined by studying the ratio of the deposition rates. In the case of sample P5-3, figure 2 confirms that ReL pyrocarbon is present at the surface of the composites whereas the proportion of SL pyrocarbon is higher at the center of the material.

### Table 2. Experimental and computed deposit thicknesses and nanotextures.

<table>
<thead>
<tr>
<th>Expt #</th>
<th>Thickness (µm)</th>
<th>Nanotexture</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5-1</td>
<td>12-7</td>
<td>12-5.5</td>
</tr>
<tr>
<td>P5-2</td>
<td>6-3</td>
<td>6-3.5</td>
</tr>
<tr>
<td>P5-3</td>
<td>13-3</td>
<td>13-4.5</td>
</tr>
<tr>
<td>P2-3</td>
<td>4-1</td>
<td>4-2.5</td>
</tr>
<tr>
<td>P0.5-1</td>
<td>4-1</td>
<td>4.5-1.5</td>
</tr>
<tr>
<td>F1</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>F2</td>
<td>37</td>
<td>37</td>
</tr>
</tbody>
</table>

Samples P5-1 and P0.5-1 were prepared for similar values of the residence time. The lower pressure applied to the latter induces a weaker deposition rate but delays the porous medium obstruction. Moreover, the deposited pyrocarbon is RL, with a high degree of anisotropy, since it originates from a defect-free lateral growth mechanism. P0.5-1 represents the best infiltration conditions.

At a given temperature, matrix properties are a result of a compromise between the pressure and the residence time. The nanotexture can be controlled through the latter: weak and important values favor formation of highly anisotropic pyrocarbons yielding better mechanical properties. However, this same quantity accelerates deposition at the surface of the preform, quickly obstructing its center to the gas phase. This phenomenon can be counteracted by lowering the pressure, therefore reducing the deposition rates and extending the infiltration duration.

**Summary and outlook**

This work focused on the modeling of the chemical vapor infiltration of pyrocarbon from propane. The presented tool first embodies a simplified kinetic mechanism leading from the precursor decomposition to the heterogeneous reactions. It also comprises an infiltration model for multi-scale computation of geometrical and transport properties. These particular computations are based on 3D CMT scans of the preforms for accurate representation of the porous structure. The resulting data from these models is incorporated into a reactor scale finite element solver and anticipates, for a specific set of operating conditions, matrix thickness and nanotexture.

The numerical infiltrations produced on carbon fiber arrangements and foams matched with experimental observations. Studies of the densification gradient singled out the influence of parameters and identified the morphological evolution of the porous medium. Guidelines for a correct
control of matrix homogeneity and pyrocarbon nanotexture have also been produced.

Ongoing efforts consist in incorporating chemical mechanisms of other precursors: methane for example, and adapting the procedure to other types of preforms.

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References