

## Numerical modeling of reactors for Chemical Vapor Infiltration (CVI) with detailed homogeneous and heterogeneous kinetics

Alberto Cuoci\*, Alessio Frassoldati, Tiziano Faravelli

*Department of Chemistry, Materials, and Chemical Engineering "G. Natta", Politecnico di Milano (Italy)*

*\*Corresponding author: [alberto.cuoci@polimi.it](mailto:alberto.cuoci@polimi.it)*

### Highlights

- A numerical methodology for modeling CVI reactors with complex kinetics was developed
- A numerical model for describing the densification process in 2D preforms was implemented
- The methodology was successfully validated in comparison with experimental data

### 1. Introduction

The Chemical Vapor Infiltration (CVI) is one of the leading manufacturing processes for production of Carbon/Carbon (C/C) composites, such as brakes. In CVI, porous preforms substrates are placed inside a reactor and are heated radiatively by the reactor walls, which in turn are heated electrically. Hydrocarbon gases, such as methane, propane, ethane, or benzene, are supplied as inlet stream to the reactor. The hydrocarbon mixture decomposes and reacts, producing several light and heavy hydrocarbons, together with hydrogen and other products. These molecules infiltrate the preform pores and react with its surfaces as well as with themselves [1]. Through this infiltration process, degradation due to interaction between the hydrocarbon gas and the solid substrate surface results in pyrolytic carbon being deposited on the surface. Over time, the preforms fill in and become denser, and ultimately form a C/C composite. The remaining gas products leave the reactor from the top. Since the substrates are heated radiatively, the gases and substrates are approximately at a uniform temperature [2]. The CVI is a complex process, in which multi-physical and multi-chemical phenomena are involved: homogeneous gas phase reactions, heterogeneous surface-deposition reactions, molecular diffusion, mixed convection gas flow, radiative heat transfer, etc. A huge range of length and temporal scales associated to the transport and chemical phenomena occurring along the reactor and inside the porous preforms can be observed. In particular, time scales vary from those associated with pyrolytic reactions (order of microseconds) to the deposition process time scales (of the order of dozens of hours). Other time scales exist between these two disparate scales, including the fast and slow chemical reactions rates, and conduction and convection time scales. In principle, a complete mathematical model has to account for most of these scales [1]. However, in practice, this cannot be realized since the span between the different scales is too large. Thus, alternative approaches have to be accounted for.

Thus, in this work we present a modeling strategy based on the partial decoupling between the evolution of gaseous phase in CVI reactors and densification process occurring over the porous substrates. The proposed methodology allows to overcome the issues mentioned above related to the existence of a wide range of time scales, without reducing the level of detailed in the description of homogeneous and heterogeneous reactions.

### 2. Methods

The CVI process is here numerically modeled by applying a partial decoupling between the pyrolysis of gaseous species inside the reactor and the densification process occurring in the porous preforms packed inside the reactor. In particular, the following two steps are carried out in series: 1) a steady-state CFD simulation of the whole reactor is performed, in which only the gaseous phase is modeled, by solving the transport equations

of mass, momentum, gaseous species and energy. No heterogeneous (i.e. deposition) reactions are accounted for and no equations are solved inside the porous preforms; 2) the CFD solution (Step 1) is used to provide the proper boundary conditions for modeling the densification process in each porous preform. In other words, once the CFD solution is available, the densification is modeled by solving the transport equations of mass, species and energy in each preform, accounting both for homogeneous and heterogeneous (i.e. deposition) reactions. The 2-step strategy summarized above is based on the assumption that the gaseous reactions occurring inside the reactor are much faster than the densification process, which is usually limited by porous diffusion, even when low temperatures are adopted. This means that the homogeneous gaseous phase can be treated as quasi-steady with respect to the densification.

Two different tools were developed to carry out the 2 steps. The CFD step (Step 1) is carried out with a customized version of laminarSMOKE code [3], a CFD code based on the OpenFOAM® framework, specifically conceived for laminar reacting flows with detailed kinetic mechanisms. The solver is able to model reactors of arbitrarily complex geometry and size, both in steady state and unsteady conditions. No limitations on the size and complexity of kinetic mechanisms are present. The densification step (Step 2) is carried out with the CVISMOKE++ solver. In its current implementation, CVISMOKE++ is able to model the densification in 2D porous preforms (planar or axisymmetric geometries), by solving the unsteady transport equations of mass, species and energy. Both homogeneous and heterogeneous kinetic mechanisms are accounted for, without limitations on their size and complexity.

### 3. Results and discussion

The proposed algorithm was validated in comparison with experimental data available in the literature. In particular, we modeled the symmetric reactor configuration experimentally studied in [4], consisting of a 2D low density (i.e. high porosity) carbon felt. Methane is supplied at the inlet of the reactor and it decomposes to produce gas phase radical species that react to form carbon particles. These particles infiltrate and are deposited inside the porous felt via a surface reaction mechanism and thus reduce the porosity in the felt. All other products leave at the outlet of the reactor. The agreement with experimental data was satisfactory. The model is able to capture, also on a quantitative basis, that bulk density slightly decreases from the outside to the inside of the felt, which is an indication of the inception of a diffusion limitation. Sensitivity analyses carried out by adding different amounts of hydrogen to the inlet stream, revealed that hydrogen addition is helpful in avoiding premature formation of crusts along the external surface of preforms.

### 4. Conclusions

A numerical strategy for modeling the Chemical Vapor Infiltration reactors typically employed for production of C/C composite materials have been proposed and implemented. The strategy allows to describe the densification process in reactors of arbitrarily complex geometry, without reducing the detail of description of homogeneous and heterogeneous (i.e. densification) reactions. Validation was carried out in comparison with experimental data available in the literature. The strategy and the developed numerical tools are currently adopted for simulating more complex and realistic CVI reactors.

### References

- [1] J. Ibrahim, S. Paolucci, *Journal for Numerical Methods in Fluids* 64 (2010) 473–516.
- [2] J. Ibrahim, S. Paolucci, *Carbon* 49 (2011) 915–930.
- [3] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, *Combustion and Flame* 160 (2013) 870–886.
- [4] W.G. Zhang, K.J. Huttinger, *Carbon* 40 (2002) 2529–2545.

### Keywords

Chemical Vapor Infiltration; carbon deposition; heterogeneous reaction; densification.