From pyrocarbon CVD to pyrocarbon CVI

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The control of pyrocarbon (pyC) CVI [1,2,3] is a key issue in the manufacturing of high-performance C/C composites with applications in aerospace parts and braking technology. For years, the precise knowledge of deposition kinetics and pyrocarbon nanotexture (*i.e.* anisotropy at nanometer scale) has been rehearsed in various reactor and process configurations, such as hot-wall or cold-wall CVD, isothermal or thermal-gradient, pulsed, forced CVI with wide variations of pore sizes and precursor gases.

Among the nanotextural types of CVD and CVI pyC, two varieties, referred to as Rough Laminar (RL) and Smooth Laminar (SL) [2,3], differ by their degree of structural anisotropy, and have distinct mechanical and optical properties [3,4]. Many experimental studies have shown in the past the importance of processing parameters [5-9]: temperature, pressure, gas phase composition, residence time (t_s), internal surface area (S_v). The most commonly accepted interpretation of the data in terms of chemical mechanism is that the precursor gases first undergo a long chain of gas-phase reactions : i) precursor decomposition, ii) recombination of the first products into other species among which unsaturated species and resonance-stabilized free radical species (RSFRs), iii) growth of heavier molecules with a varying degree of unsaturation or aromaticity (among which PAHs – Polycyclic Aromatic Hydrocarbons, and polyynes). Then, all of the produced gas-phase species are susceptible to yield a pyrocarbon deposit ; the nanotexture of pyC is believed to rely on the ratios between these species.

One of the most confusing points is that CVD observations and models are not readily transposable into CVI models, first because of the high S_v values, and the important role played by heterogeneous chemistry in CVI, in contrast to CVD, and also because of the depletion effects that are to be expected in narrow pores. A starting point for our investigations is the series of experimental studies performed at LCTS [8] using a tubular reactor at P = 2 kPa, T between 1100 and 1300 K, t_s in isothermal hot zone from 4 s. down to 0.5 s, and pure propane as a precursor, and for which a 1D model with detailed chemistry has been designed and validated [10]. Correlation between FT-IR and GC-MS measurements, concentration computations, CVD growth rate and deposit nanotexture analyses strongly suggested that the SL and RL pyC varieties could be respectively associated to light (group B) and heavy (group C) hydrocarbons. A simple kinetic model featuring a threshold pressure for group C species in order to represent its appearance at large residence times, has been able to reproduce the experimental CVD growth rates.

Such a model has then been tested against CVI experiments in model pores (S_v ~30000 m^{-1}), for which deposit thickness and nanotexture were inspected as a function of pore depth. The pore mouth thicknesses were always in agreement with CVD runs in equal conditions, which allows to infer that the retroaction of the porous medium on the gas-phase chemistry was not strong. The thickness profiles always displayed neat slope breaks after a few micrometers in depth, a fact that had been reported previously [7,9]. From such a fact, it has been necessary to consider splitting the group B species into several groups (fig. 1) : an inert group B0, a strongly reactive group B1, present in small amounts, and a much less reactive group B2, present in larger amounts. By comparison with 1D pyrolysis computations, it appears that methane and ethane are good candidates for B0 group, while acetylene would be appropriate for B2, and B1 would be either a radical or a heavier hydrocarbon. Going back to CVD, the enhanced model maintained correct agreement. This illustrates the fact that CVD experiments are not able alone to provide a good enough guess for CVI reactions.

Considering now other precursors than propane, some transpositions are easily guessed by use of the 1D pyrolysis computations. Using propene instead of propane will lead to shift all models towards lower residence times, because propene is one the first by-products of propane decomposition at high temperatures. Indeed, this fact has been confirmed experimentally. Also, using methane instead of propane will lead to an opposite shift towards high residence times : this is due to the very low reactivity of methane, which requires a long induction period before yielding in appreciable amounts reaction intermediates like unsaturated C2 species, which will then follow approximately the same reaction pathways as in the case of propane. For this reason, it is not surprising that deposit thicknesses increase with pore depth in reported cases of CVI from methane[11].

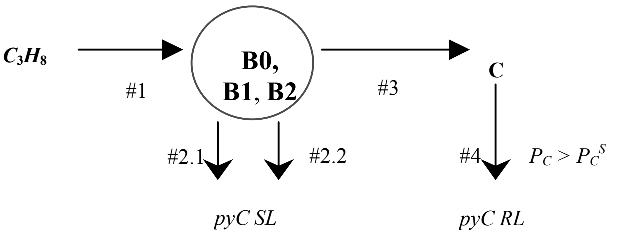

Figure 1 : a CVD/CVI model for pyC deposition from propane.

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