

THE CONTROL OF INTERPHASES IN CARBON AND CERAMIC MATRIX COMPOSITES

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ABSTRACT:

Toughness and damage-tolerance of ceramic matrix composites (CMC) are achieved by engineering the fiber/matrix interface in order that a crack initiated in the brittle matrix does not propagate in a catastrophic manner through the reinforcing fibers. Since the 1970s, many solutions ranging from simple interface response to addition of a monolayer or multilayered interphase have been imagined and developed. Among them the pyrocarbon (PyC) interphase may be considered as a reference. However, its performance is highly dependent on its nanotexture that has to be accurately tailored through its fabrication process: chemical vapor deposition or infiltration (CVD/CVI). Control of pyrocarbon microstructure by CVI is a key issue in the processing of PyC interphases in CMC as well as of matrices in high-performance carbon/carbon composites. The gas-phase chemistry plays a key role in the various nanotextural transitions. The relation between nanotexture and processing conditions has been elucidated by joint experimental and modeling approaches.

KEYWORDS: fiber/matrix interphases, CVD of Pyrocarbon.

INTRODUCTION

Although man knows empirically for thousands of years how to improve the behavior of brittle materials such as straw-reinforced mud bricks, or more recently to improve the mechanical properties of materials by use of a composite structure (Mongol bow), the controlled elaboration and further understanding and improvement of ceramic matrix materials are only 40 to 50 years old. Carbon/carbon (C/C)¹ and ceramic matrix composites (CMC)² are nowadays used to produce at an industrial scale, parts of rockets or aircrafts: engines nozzle, divergent skirt, heat shields for atmospheric reentry, brake discs... These materials are furthermore aimed at being used in civil aeronautics to replace an increasing number of metallic parts: aircraft engine plug or exhaust, compressor blades...).

In order to allow these composite materials to become reliable and reproducible industrial products, several main issues had to be overcome. Among them, the first difficulty was to find a way to confer a reasonably tough and damageable behavior to a composite material that comprises exclusively brittle constituents. CMC differ significantly from other types of composites as the failure strain of the matrix is lower than that of the fiber. For that reason, they are called inverse composite as compared to metal/metal composites (MMC) or organic matrix composites (OMC): under tensile load in the direction of the fibers, the matrix fails first. Back to the mid 1960s Cook & Gordon³ stated that "Inside a brittle solid, if a plane of weakness or potential cleavage is present and is roughly normal to the plane of the original crack, this interface may break and produce a secondary crack in such a manner as to interfere with the progress of the primary crack."

It is now well established that the mechanical behavior of such materials is critically dependent on the bonding between fiber and matrix and it has been further demonstrated that this bonding is also critical for oxidation resistance of the composite at high temperature in oxidative environments. This property gives the specific added value to fibers embedded in a matrix: the whole is greater than the sum of the parts. However, in order to be efficient, the bonding has to be adjusted at the "proper" value: if the fiber/matrix (F/M) bonding is of the same order of magnitude

than that of the matrix, it is called strong and the composite is brittle; in contrast, if the F/M bonding is weaker, the composite becomes non-brittle. Of course, if it is too weak, then the matrix plays no role in the composite. In other words, the strength of the bonding must be sufficiently high to allow an efficient transfer of the load applied to the matrix, towards the reinforcing fiber, but sufficiently weak to prevent the cracks generated in the matrix to propagate through the fiber and induce the ruin of the composite.^{4,5}

After a short review of the various interphases that can be used in SiC/SiC composite materials, the present paper will focus on the understanding of the chemical processes leading to the formation of the large variety of pyrocarbon nanotextures (or microstructures). The control of the pyrocarbon microstructure is a main issue of the CVD/CVI process both for SiC/SiC (interphase) and Carbon/Carbon composites (matrix). The influence of the process on the structure and properties of the deposited pyrocarbon are detailed. The influence of the nature of the precursor is discussed.

INTERPHASES IN SiC/SiC

The F/M bonding is indeed not a surface or interface which could be understood as a pure 2D domain. As the result of physicochemical processes (chemical reaction, diffusion) that takes place at high temperature, it is usually composed of one or many thin phases. These phases may form a third body between fiber and matrix or extend themselves inside the fiber. A huge amount of literature has been devoted to the characterization and understanding of a domain the thickness of which typically ranges from 10 to 100 nm, and has accordingly to be investigated at nanometer scale. Readers are referred to a review⁴ on the subject and we only mention here the main milestones.

The simplest bonding approach is to promote and control the formation of a weak interphase during the high temperature step of the processing. This approach has been used for the development of glass-ceramic matrix composites⁶. First generation Si-C-O fibers that contain excess carbon and oxygen form a carbon rich fiber/matrix interfacial layer when incorporated into glass-ceramic matrices at elevated temperatures, which is responsible for the high toughness observed.

Another approach is based on the deposition of a thin coating on the fiber prior to its densification stage to form the matrix. As the additional phase may be designed as a single layer or a multilayered coating, it offers much more flexibility. A large variety of phases or combination of phases has been applied to C/SiC and SiC/SiC composites. The most commonly used are materials exhibiting a layered crystal structure: PyC, hex-BN, BCN⁷. However, PyC is prone to oxidation above 500°C, hex-BN is moisture sensitive when prepared at low temperature and BCN is difficult to prepare at a desired composition. Other phases exhibiting a layered crystal structure and showing furthermore a good oxidation resistance belong to the MAX-phase family. Their interesting combination of properties is traceable to their layered structure, including a combination of mostly metallic strong M-X bonds, together with relatively weak M-A bonds allowing shear cleavage. The ternary most-studied as interphase to date is Ti₃SiC₂^{8,9}. However, as a CVD deposit, it has been up to now unable to deflect cracks, since its layered structure has not been obtained parallel to the fiber surface. The concept of intrinsic nano-layered material has been extended to stacks of layers made of different materials^{4,5}. Such a concept allows a wide choice of materials that can be tailored to deflect cracks and/or improve oxidation resistance behavior, either by use of oxidation resistant materials or by formation of healing materials. Though a large variety of different layers can be associated, thus generating a wide field of new fiber/matrix interphases, such nanometer-thick multilayered structures are difficult and expensive to control at an industrial scale. Several examples are encountered in the literature, many of them having been summarized in reference 4.

PYROCARBONS

Among all the interphases described above, pyrocarbon or pyrolytic carbon¹⁰ is still, in spite of its poor oxidation resistance, a reference material. It is obtained by dehydrogenation at high temperature of a gaseous hydrocarbon. For CMC or C/C fabrication purposes, it is usually grown by CVD or CVI process on a hot fibrous substrate. The structure of pyrocarbon is similar to that of graphite but includes disorder (figure 1): graphene layers have limited extent and may include C5 or C7 arrangements responsible for some waviness; they may furthermore be stacked with rotational disorder (turbostratic graphite) and contain screw dislocations.

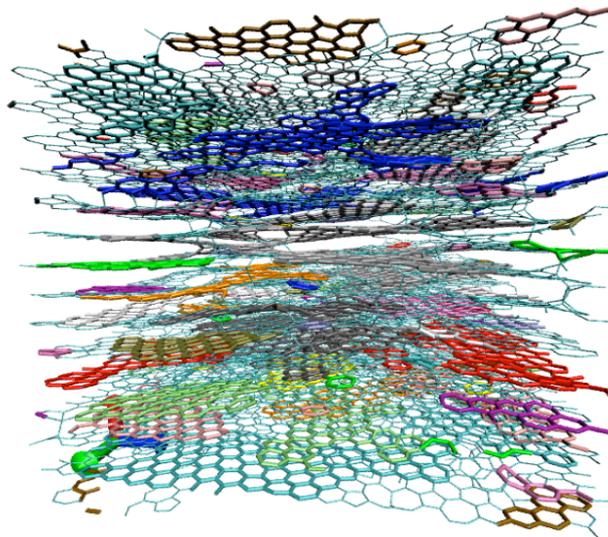


Figure 1: Atomistic model of pyrocarbon obtained by Image Guided Atomistic Reconstruction (IGAR) method¹¹

The versatility of disorder features leads to various nanotextural forms of pyrocarbon¹²⁻¹⁶, ranging from nearly isotropic to highly anisotropic (*i.e.* close to graphite structure). Various denominations are encountered according to distinct scientific and technological teams. The characterization of PyC nanotexture and its relation to processing conditions have been the object of investigations since more than 50 years.

A key issue in the CVD or CVI of pyrocarbons is the control of the nanotexture of the deposit during processing. In the case of SiC/SiC interphase, the graphene layers have i) to be oriented parallel to the fiber surface, and ii) to form a bond with the fiber surface, which must be strong enough in order that the debonding induced by crack deflection occurs at the interphase/matrix interface. In the case of carbon/carbon composites, the basic questions to be addressed are i) how to obtain a uniform dense matrix in the preform in a reasonable time, ii) how to control the homogeneity of the microstructure through the whole thickness of the part to be infiltrated. For both applications, another question is which carbon precursor to choose among the numerous potential hydrocarbon molecules. Though easy to implement, the CVD/CVI process is extremely complex as it involves numerous homogeneous as well as heterogeneous chemical pathways, both in the reactor and in the preform, fluid flow, heat and mass transfer. Accordingly, the basic need of understanding in order to optimize the fabricated material is high. CVD and CVI pyrocarbons have been the object of studies since many decades and is still a topic of actuality, because of the complexity of the involved chemistry, and of its subtle entanglement with transport phenomena.

Starting in the early 1960s, the main improvements concerning CVD/CVI of matrices in C/C composites have been recently reviewed by R.J. Diefendorf¹⁷. The paper discusses the merits of the

various types of CVI processes: isothermal or with temperature-gradient, with or without forced or pulsed flow. It also addresses the thermodynamics of the carbon/hydrogen system. Soon¹⁸⁻¹⁹ he had recognized that, starting from methane, temperature and pressure were critical parameters influencing the organization of the deposited carbon. For example, fig.2 shows¹⁸ – in the case of CVI from methane – the distinction between isotropic (sooty) carbons and anisotropic (laminar) pyrocarbons, the first ones being the result to some extent of homogeneous nucleation, while the second ones were more linked to heterogeneous processes. However, this description is highly dependent upon reactor geometry and residence time and has accordingly been subject to strong controversies.

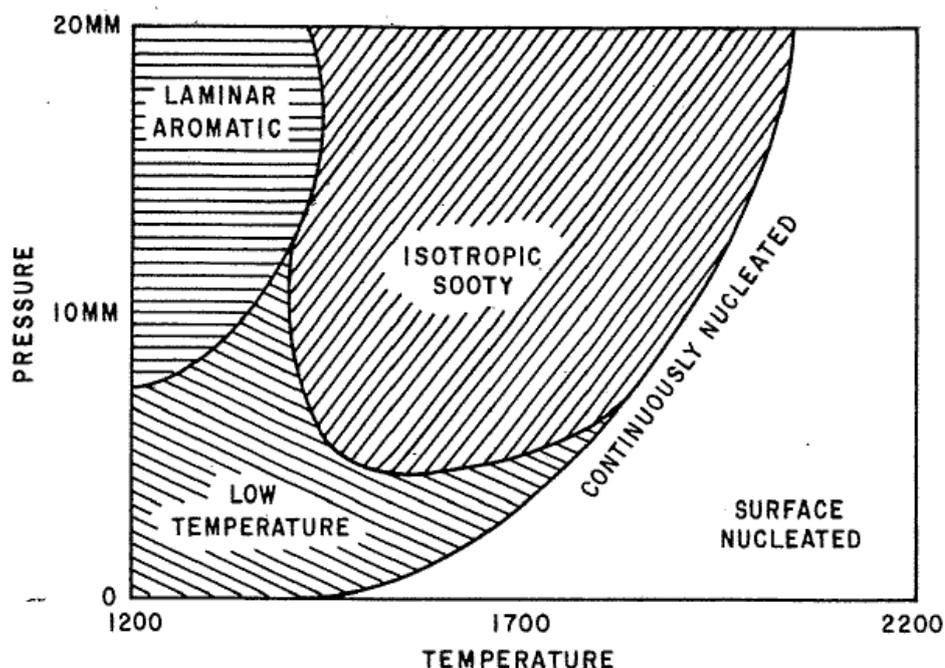
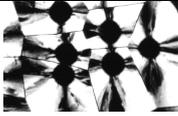
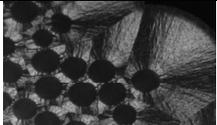
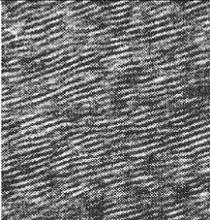
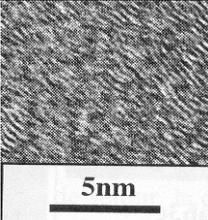
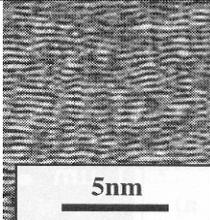
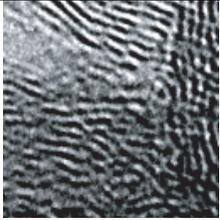
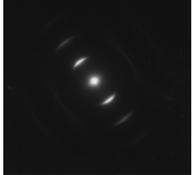
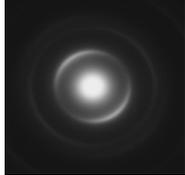
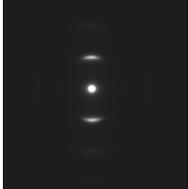


Figure 2: Fields of microstructure for pyrolytic graphite deposited from methane according to ref. 18

Some time later, several kinds of laminar pyrocarbons were distinguished.^{20,21} Among them, two varieties have been identified, and have been called “Rough Laminar” (RL) and “Smooth Laminar” (SL) because of their appearances when imaged by Polarized Light Optical Microscopy (PLOM), as described by Diefendorf & Tokarsky²²: when rotating the cross-polarized light, the orthogonal branches of the Maltese cross show a ‘rough’ extinction in the case of Rough Laminar variety, though extinction is ‘smooth’ in the case of smooth laminar variety. Rough and smooth PyCs differ by their degree of structural anisotropy, and have distinct properties. For instance, the RL form is graphitizable by a high-temperature post-treatment^{13,14}. Much more recently, a new form of highly anisotropic PyC, distinct from RL, has been identified and termed “Regenerative Laminar”.²³ Raman analysis under polarized light has played a crucial role in separating these forms from each other.²⁴ Confusion between RL and ReL has been common until very recently. There are still classifications which are only based on the optical or Small-Area Electron Diffraction (SAED) anisotropy^{25,26} and do not provide a distinction between RL and ReL.

The current state of pyrocarbon denominations, together with a detailed description based on PLOM imaging, extinction angle, High Resolution Transmission Electron Microscopy - Lattice Fringe (HRTEM - LF) imaging, SAED Opening Angle, and Polarized Raman signals, is summarized in Table 1.

Table 1. Classification and description of pyrocarbons, in relation with processing parameters.

Recommended name ¹⁵	Rough Laminar (RL)	Smooth Laminar (SL)	Regenerative Laminar (ReL) (was formerly confounded with RL)	Dark Laminar (DL)
PLOM visualization on fibers and extinction angle (Ae°)	 [15-23]	 [10-14]	 [15-23]	 [5-10]
HRTEM LF visualization				
SAED figure and Opening Angle OA°	 [20-40]	 [40-90]	 [20-40]	[80-90]
Raman anisotropy ratio R _A (-)	[5.5-10]	[4-5.5]	[5.5-10]	[4-4.5]
Raman band width FWHM _D (cm ⁻¹)	[80-140]	[80-200]	[140-200]	[80-200]
Graphitizable ?	Yes	No	Yes	No
ICT Karlsruhe classification ²⁵⁻²⁶	High Textured (HT)	Medium Textured (MT)	High Textured (HT)	Low Textured (LT)
F. Langlais <i>et al.</i> Classification ⁵⁸	Columnar Laminar (CL)	Weakly Anisotropic Laminar (WAL)	Highly Anisotropic Laminar (HAL)	Quasi-Isotropic Laminar (QIL)
Processing conditions	 Increasing T ; increasing t_s ; decreasing S_V ; increasing hydrocarbon source gas reactivity			

PYROCARBON NANOTEXTURE: PARAMETER INFLUENCE AND MECHANISM

It has been shown^{18-21, 27-29} that the most influential processing parameters are, in addition to temperature T and pressure P , and initial gas-phase composition: residence time t_s and deposition space volume/deposition surface area ratio, S_V ³⁰. One of the most confusing points is that CVD observations and models are not readily transposable into CVI models, for at least three reasons. First, because of the high S_V values, heterogeneous chemistry plays a much more important role in CVI in contrast to CVD³⁰. For instance, if saturation adsorption may occur in CVD, this is much less possible in CVI, at least far from the porous medium surface. Also, some pyrolysis sub-mechanisms which exist in the gas phase may be completely overridden by heterogeneous ones, leading to a very different apparent behavior of the gas phase. Second, depletion effects are to be expected in narrow pores, due to transport limitations. This latter point has been thoroughly investigated in numerous modeling works, dealing either with isothermal-isobaric CVI (I-CVI),³¹⁻³⁴

forced-CVI (F-CVI),³⁵ thermal-gradient-CVI (TG-CVI) -- either with microwave or radio-frequency heating (see a review in Ref. 36). Third, the depletion effects that are to be expected outside the fibrous preform may be very pronounced in CVI cases that correspond to very high S_V values.³⁷ The preform is much more reactive than a plane substrate, so that the diffusion boundary layer which surrounds it is larger, and may easily reach the outer walls.³⁸ Taking these facts into account is only feasible in a global modeling frame where both the preform and the surrounding free-medium are simultaneously considered.³⁹

Many experimental studies have shown in the past the importance of processing parameters on the PyC deposition rates and nanotexture, in various physico-chemical conditions and reactor configurations, either in CVD (plain substrate, low S_V), or in CVI (porous substrate, high S_V).⁴⁰⁻⁵⁸ Most of them have tried to identify some “ultimate precursor” of PyC, either light, aliphatic species, or heavy aromatic compounds such as Polycyclic Aromatic Hydrocarbons (PAHs) and polyynes. It has been proved, from mass spectroscopy,^{49,53,29} gas chromatography,^{54,55} and FT-IR^{56,57,58} measurements of the gas-phase composition, that the hydrocarbon pyrolysis follows a long chain of homogeneous reactions, in a so-called “maturation” process : 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.

One the key issues of pyrocarbon nanotexture control is the identification of the most important species and sub-mechanisms that may be associated to a given nanotexture. R.J. Diefendorf⁵⁹ contributed to the pioneering work devoted to the understanding of the various mechanisms involved in the deposition of pyrolytic carbon. He was among the first to identify the influence of gas phase mechanisms on the switching between distinct growth processes: either growth from the edges or deposition on the surface of basal planes, according to the nature of the molecules formed in the gas phase. In the case of heavy precursors, a condensation-like mechanism has been proposed,^{59,60} while for light species, a lateral growth mechanism, close to a radical-based polymerization reaction scheme, are more likely.^{59,61} It has to be expected that the overall reaction rate dependence on temperature should vary with temperature (since the activation energies may be different), on the total pressure and residence time (since the relative amounts of various key species may vary), and on S_V (since the heterogeneous to homogeneous reaction ratio varies). Indeed, all these parameters may toggle the system between various dominant mechanisms.

Actually, the experimental data, as collected from propane and methane pyrolysis and subsequent CVD, were puzzling. Fig. 3 summarizes the numerous textural transitions that have been observed in methane^{62,63} and propane^{55-58,64-66} pyrolysis.

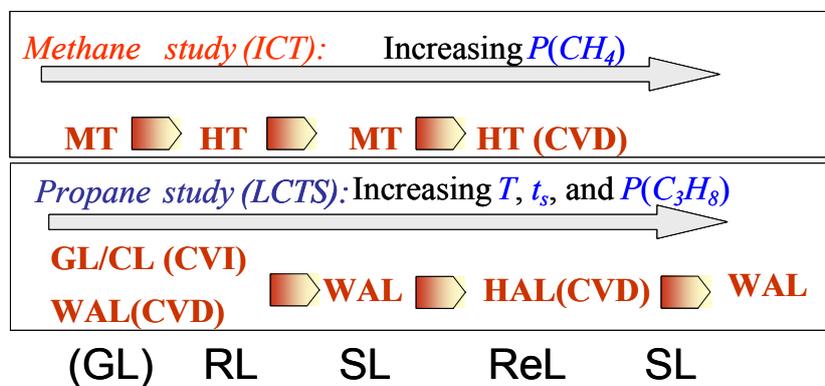


Figure 3: Observed textural transitions in methane studies at ICT^{62,63} and propane studies at LCTS.^{55-58,64-66} Notations are explained in Table 1.

In both cases, when processing parameters acting directly on gas-phase maturation are varied, there is a non-monotonous evolution of the anisotropy degree. The only point is that sometimes the data from distinct authors were in apparent contradiction. Guellali⁶² reported in model capillaries (moderate S_V , close to CVD conditions) a “(low-)high-low-high” anisotropy sequence while in CVD Féron^{56,57} reported a “low-high-low” sequence. At first, no attention was paid to distinguish between RL and ReL (both being highly anisotropic). Later on, it was understood that the second highly anisotropic PyC appearing in the propane study was ReL as opposed to RL at low residence times and high S_V ratios. Things went thus clearer when LCTS managed to produce highly anisotropic PyC at extremely short residence times: it was RL and not ReL. The anisotropy evolution sequences could then be matched as depicted in figure 3.

PYROCARBON DEPOSITION: MODEL BUILDING

From a chemical kinetic point of view, the modeling efforts concerning PyC deposition have been devoted primarily to the study of the maturation phenomenon, that is, to hydrocarbon pyrolysis. The gas-phase reaction steps have been successfully modeled using comprehensive⁶⁷⁻⁷¹ or semi-detailed⁷² mechanisms. They have been completed by the incorporation of heterogeneous reactions,⁷³⁻⁷⁴ but with less detail due to the lack of knowledge concerning these reactions.

In the case of propane decomposition at $P = 2$ kPa, $T = 900^\circ\text{C}$ - 1200°C , and moderate to large residence times, in a CVD tubular reactor, a kinetic modeling study based on a detailed gas-phase mechanism has confirmed the maturation phenomenon and its importance on the transition from SL to ReL (mistakenly called RL in the papers) when residence time and/or temperature increases.^{67,68} It appeared that only the heaviest species in the detailed model could account for ReL pyrocarbon growth, while many lighter ones were related to SL. A very detailed study has been devoted later on to the growth of SL pyrocarbon,^{69-71,73,74} and one of the results is that SL PyC growth is equally due to the presence of CH_3 radicals and C2 molecules like acetylene and ethylene.

A CVD simplified model has been deduced from the detailed pyrolysis study⁶⁸ in order to define a computationally tractable chemical model to be included in the full scale modeling of the reactor. Its simplified homogeneous chemical path takes into account two groups of key species: aliphatic species (mainly CH_4 , C_2H_6 , C_2H_2 , C_6H_6 according to the initial hydrocarbon molecule) that contribute to the growth from the edges of carbon basal planes, and PAHs species that contribute to the growth of the surface of carbon basal planes through a condensation-like mechanism. Note that the kinetic constants associated with the formation of intermediate aliphatic species CH_4 and C_2H_6 or C_2H_2 or C_6H_6 takes implicitly into account the whole detailed gas-phase mechanism including intermediate species. For that purpose, experimental data have been used for the identification of some rate constants and activation energies. It is worth noting that this CVD model accounts for the last $\text{ReL} \rightarrow \text{SL}$ transition at large residence times, due to PAH depletion. For the full-scale modeling of the CVI reactor including the simplified chemical model,^{38,75} the porous medium model was such that its effective transport coefficients were known precisely enough during infiltration. Thus, one-dimensional CVI computations have been performed in order to reproduce the deposit thickness profiles. The model manages to reproduce successfully either CVD or CVI experiments using propane. This model has also been injected into a coupled solver featuring both free-medium and porous medium, and allowed to understand how ReL PyC appears by maturation then disappears by depletion due to the large deposition rate of PAHs. Deposition experiments in carbon foams, with moderate S_V ratios, were successfully modeled.⁷⁶

In the case of PyC deposition from methane, the detailed models of pyrolysis⁷⁷ show that the characteristic induction times for maturation are considerably higher than those for propane, due to the exceptional stability of the methane molecule. This arises from the high activation energy for C-

H bond breaking, which is crucial in the first step of methane decomposition chemistry. Additionally, this first step is a “third-body enhanced” reaction:



which gives an important role either to total pressure or to S_V (M being any gaseous species or the surface, respectively). This special feature of CH_4 has been successfully used to undertake inside-out isothermal CVI.⁷⁸ Once the pyrolysis has begun, attention is paid mostly to acetylene and benzene as key intermediates for the growth of PyC at low residence times, and PAHs for large residence times. This is in complete consistency with the propane-based chemical scheme.

More recent simulation studies^{79,80} with parameter identification based on CVD⁵¹ and CVI^{54,30-31} experiments tend to confirm the idea that groups of molecules C_2H_2 , C_6H_6 and PAHs are also key species in the case of deposition from methane. The main difference is now that CH_4 should be considered both as the initial hydrocarbon molecule for the mechanism as well as an intermediate species; the formal scheme presented for propane does not have to change, only the H_2 production stoichiometry has to be revised.

There remains to explain why highly anisotropic PyC is deposited at very short residence time and high S_V ratios, and this is more complicated. Low molecular weights molecules are obviously involved in the process and there is strong evidence that key species have to be early products of pyrolysis (first- or second-generation products, like the CH_3 radical, C_2H_4 , etc ...).

It has been argued that HT deposition from methane (probably RL) results mainly from aliphatic species, since, at the considered experimental conditions (higher P and T), homogeneous nucleation of soot overrides the formation of HT PyC. To explain this, a “particle-filler” model has been proposed,⁷⁹ asserting that the degree of anisotropy is susceptible to increase when a particular $\text{C}_2\text{H}_2/\text{C}_6\text{H}_6$ ratio is reached, this phenomenon taking place at short residence times. This model states that very anisotropic pyrocarbon may be deposited by lateral growth of graphene planes, for which the lowest quantity of defaults (e.g. C5 or C7-rings, helicoidal structures) is attained when C_2H_2 acts as a “filler” between C_6H_6 “particles”. However, it is difficult to imagine the precise bimolecular or multi-molecular mechanism through which C_2H_2 and C_6H_6 would yield perfectly matching additions. Numerical results from the detailed mechanism⁸⁰ also give two pieces of information on the propane and methane cases: first, C_2H_2 and C_6H_6 have a very similar variation, even though C_6H_6 is formed later; second, the $\text{C}_6\text{H}_6/\text{C}_2\text{H}_2$ ratios correlated to RL deposition are neatly different in the two cases. There is no obvious explanation for this latter fact with the “particle-filler” model.

On the other hand, there have been tentative explanations based on the topology of carbon edge growth from molecules and radicals containing even or odd numbers of carbon atoms. In the case of propane, it has been proposed⁸⁰ that the very early stages of decomposition (or no decomposition at all) favor the relative abundance of C3-containing species, while later stages of maturation increase the C2-containing species amounts; in his review¹⁷, R. J. Diefendorf suggests that C2 species are capable of creating C5 cycles, and consequently local bending of the graphitic sheets.⁸¹ This fact is also consistent with the RL→SL transition in the case of methane – indeed, detailed modeling yields CH_3 as a first radical, and C_2H_2 appears much later during pyrolysis; if CH_3 is dominant in the gas-phase, then hexagon growth is preferred and the anisotropy is large, while if C_2H_2 dominates, then faulted cycles are more abundant and the anisotropy decreases.

Thus, a global model of PyC deposition should take into account the gas-phase maturation (i.e. the onset of various species by bond breaking and recombination), and deposition mechanisms originating in various precursors, since the non-monotonous anisotropy transitions clearly suggest a variety of heterogeneous reactions. Concerning homogeneous reactions, it seems that propane and methane show a similar behavior, at the noticeable exception of the initiation step, which is much slower for methane.

First, highly anisotropic PyC deposited at long residence time (ReL) is clearly related to high molecular weight species such as PAHs as established both from experimental⁵⁵⁻⁵⁸ and computational^{68,75} facts. In contrast, the intermediate MT (SL) and low-residence time HT (RL) forms of PyC seem to be correlated to species with lower molecular weights,^{69-71,73,74} the presence of C₂H₂ (and C₆H₆) inducing a loss of anisotropy and triggering the RL → SL transition.

The qualitative schemes of the propane-based and methane-based mechanisms for PyC deposition are summarized in figure 4. A companion paper⁸² discusses its identification and implementation, with a successful validation with respect to experimental data in the case of propane pyrolysis.

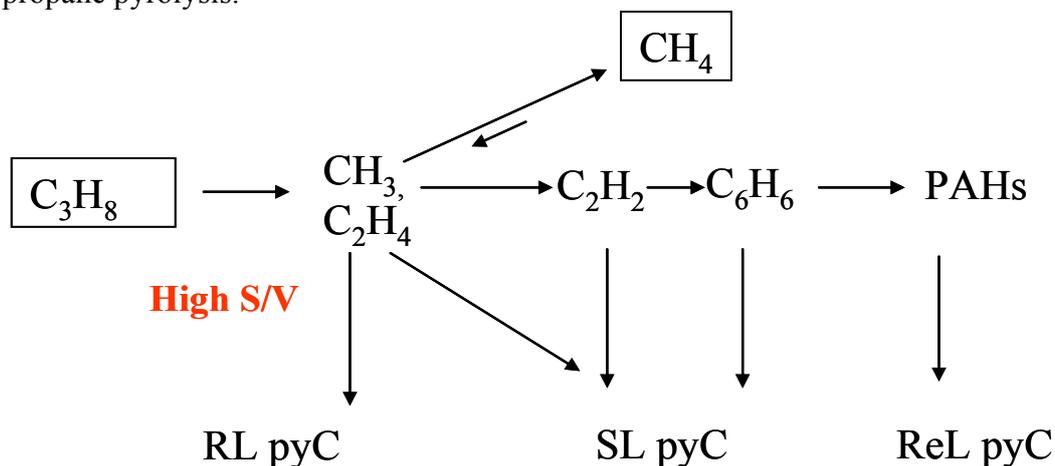


Figure 4: simplified homogeneous chemical path deduced from the detailed mechanism.

CONCLUSION

This document has summarized some key aspects in CMC and C/C composite development to which the contribution of R. J. Diefendorf has been of large importance for the scientific and industrial community. His ideas have been starting points and guidelines for many studies which have led to the current state of knowledge on interphases, and principally pyrocarbon ones.

Though pyrocarbon, almost exclusively composed of carbon (and less than 1at% hydrogen), can be seen as the simplest material for matrix or interphase purposes, it shows many varieties of textures that have to be controlled. Indeed, the ability of PyC to graphitize or to show some desired properties requires specific nanotexture that must be tailored by the manufacturing process. Materials science has taught us the exclusive relationship between a process and the properties of the produced material. Apart from the usual parameters controlling the process (T , P , initial gas-phase composition), two parameters are of critical importance in the growth of PyC from chemical vapor deposition: residence time and deposition space volume/deposition surface area ratio. Both are related to homogeneous gas phase reactions during their transport towards the surface to be coated and their competition with heterogeneous reactions responsible for the growth itself. Accordingly, the understanding and control of the desired PyC properties requires in this case an extended knowledge ranging from solid state chemistry to gas phase reactivity by relying on chemical engineering.

Even though the control of the pyrocarbon nanotexture, and thus of the composite toughness is now at hand, there is still work to perform on the subject, both from the industrial side – process optimization, control of manufacture – and from the basic science side – for instance, heterogeneous chemistry modeling is still in its infancy when one deals with such a fascinating material as pyrocarbon.

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