CHEMICAL VAPOR INFILTRATION PROCESSES OF CARBON MATERIALS

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1 Introduction

Monolithic carbons as well as thin films or carbon–carbon composites are prepared from pyrolysis and consequent carbonization of an initial organic phase. Compared to bulk pieces these composites present a noncatastrophic failure under severe experimental constraints: this is the basic reason for their broad applications (Delmonte, 1981). Before going into the details of the different processes and the associated composites manufacturing it is note-worthy to remind some basic concepts on carbon deposition. Indeed the structures and properties of a deposited carbon or pyrocarbon are related to the pyrolysis conditions which control the mechanisms of carbon formation. The matrix precursor can be either liquids or gases; in the first case the process is labelled as the impregnation technique starting usually from fluid resins or pitches (Rand, 1993). The second process is the cracking of a hydrocarbon gas at high temperature under an inert atmosphere. The associated coating process on hot bulk surfaces is called the chemical vapor deposition (CVD) and alternatively on porous substrates the chemical vapor infiltration (CVI) technique.

In this chapter, we will examine mainly the thermal decomposition of an hydrocarbon gas, the most versatile deposition process, which is widely used to make carbon–carbon composites; starting from a porous preform made of shopped or continuous carbon fibers, arranged in different bundles arrays, which are usually ex polyacrilonitrile (PAN) type. These composites are realized by filling all the voids of these preforms with an adapted fiber–matrix interaction (Inagaki, 2000).

This presentation will start with a comparison between the CVD and CVI processes including the historical aspects which have been introduced a long time ago.

Both techniques are based on the competition between the chemical reactions and the physical transport properties as discussed in Section 2. Then in Section 3 we present the different processes starting from pioneering works in the sixties until the more recent improved processes. Several new approaches have been developed these last years to optimize the infiltration processes and to understand them keeping in mind that the two key points are to speed up the deposition efficiency and to ameliorate the deposit quality of the matrix.

In Section 4, the approach will deal with the study of the formation of pyrocarbons, their different microstructures described at different length scales and their growing stability.

They are functions of different external parameters that we will analyze to establish a relationship between the deposition mechanisms and the structural and physical properties of the matrix. These pyrocarbons will be defined as a subclass of non-crystalline graphitic carbons (Delhaès, 2000). In Section 5 some basic concepts regarding a few infiltration models are presented; our approach starting with thermodynamics equilibrium at the first level is relevant to out-of-equilibrium modeling. The main emphasis will be about the competition and the interactions between the chemical kinetics and the transport coefficients in a porous medium. Dynamic modeling of CVI processes result from these theoretical works.

Finally the physical properties and the numerous applications of carbon–carbon composites are summarized. They are related to their peculiar characteristics – light weight associated with high mechanical strength including stiffness, wear, toughness, and thermal shock resistance.

2 General background on CVD and CVI processes

2.1 Definitions and outlines

The different types of allotropic forms for crystalline as well as non-crystalline carbons are essentially functions of two basic parameters. They are the nature and phase of the precursor and the experimental method selected to deliver the process energy respectively (Delhaès and Carmona, 1981). Indeed the final product, except hexagonal graphite, is in a metastable thermodynamic state which needs to be defined. Two main classes of precursors exist, either pure solid carbons or various gas and liquid hydrocarbons containing possibly hetero-elements as oxygen, nitrogen or even halogens. In the first case, this is a physical process as produced by thermal or laser beam evaporation, ion-plasma techniques as electrical discharges or sputtering techniques. Starting from hydrocarbon precursors rather complex chemical processes are ocurring including the pyrolysis and carbonization steps to obtain a pyrocarbon coating. In that situation the supplementary energy is also afforded by similar techniques but the control of the complex and numerous chemical reactions is essential. This is the natural approach for CVI processes that we are developing in this chapter. Following a chronological approach it is necessary to remind that the main point is to control both the homogeneous gas phase reactions and the heterogeneous ones at the solid-gas interface, and thereafter the deposition mechanism on a selected substrate. Many studies have been accomplished to understand the mechanism of carbon formation from different gaseous organic compounds (Tesner, 1984) and to establish a relationship between the deposition conditions and the structures of pyrocarbons (Bokros, 1969). Before going into the details of the physical process which can be defined as a balance between chemistry and hydrodynamics we will introduce the basic chemical mechanisms which have been established with some emphasis on the progress gained during these last years.

2.2 Chemistry of carbon formation

We summarize both the mechanisms and kinetics of the overall reactions. In general the precursors are alcanes, usually methane or propane, but also non-saturated hydrocarbons (such as acetylene or propylene) or aromatic molecules (benzene and derivatives) which are decomposed at a lower temperature than the alcanes. From all the experimental studies it results that a general trend can be drawn to furnish an overall reaction modeling which consider two main classes (Hüttinger, 1998). *Homogeneous gas phase reactions* The radical processes are favorized, the primary and secondary mechanisms give birth to free radicals which are recombined immediately. In a first step non-saturated species (as allenes, propyne, butadiene) are formed. Following the formation of these aliphatic compounds different cyclization processes occur; there are mainly the C_3 and C_4 cyclization ways and the HACA (H abstraction and C_2H_2 addition) mechanisms (Frenklach, 1996). Aromatics and polyaromatics (HAP) are formed for a longer reaction time (Lucas and Marchand, 1990). This is the so-called maturation effect involving the aromatic route which depends on the residence time of the molecules in the free reacting volume (Ferron *et al.*, 1999). In situ spectroscopic analysis have been carried out to follow both the mechanisms and kinetics of these complex reactions (Chen and Back, 1979; Ferron *et al.*, 1997). They give valuable information but no definite results for the complete understanding of the pyrocarbon deposition. Indeed the active species are essentially free radicals which are instable (life-time about 0.01 sec). The stable molecules which are side products, not directly transformed in solid carbon, are preferentially detected by these different analytical techniques as mass spectroscopy or gas chromatography.

Heterogeneous surface reactions They are fundamental for the formation rate of pyrocarbons, starting from the nucleation and the growing processes on a given substrate. These interfacial reactions, associated with sticking coefficients and surface migrations, specific for each species, have been investigated for a long time (Tesner, 1984); they are very difficult to analyze and therefore to control. One attempt has been to consider Langmuir–Hinshelwood model for the kinetics of surface reactions (Benziger and Hüttinger, 1999a,b). In particular, the influence of catalysts as transition metals and additive reacting gas are predominant factors. For example, hydrogen but also oxygen or chlorine gas play a role for both the deposition mechanism and the type of deposit.

Starting from the initial works (Diefendorf, 1960; Tesner, 1984) many studies have been done to understand the intrinsic mechanisms but with a rather small insight for the details of the chemical roads which remain a current challenge.

In conclusion, without taking account of the specific nature of the pristine gases, a summary of all the possible generic radical type reactions is given on the schema presented in Fig. 5.1 (Hüttinger, 1998). The chemistry inside the homogeneous gas phase leads to the aliphatic formation (C_2) as ethylene or acetylene, then the aromatic route (C_6) of benzene type species, and the formation of polyaromatics, then droplets in the gas phase (homogeneous nucleation) when the residence time is long enough (Grisdale, 1953).

This is in qualitative agreement with the thermodynamic calculations at thermal equilibrium concerning acetylenic and aromatic species carried out with thermodynamic softwares



Figure 5.1 Simplified reaction scheme for pyrocarbon deposition; the rate constants are labelled (Ki) (adapted from Hüttinger, 1998).

for methane (Lieberman and Pierson, 1974) and other hydrocarbons (Diefendorf, 1969) and confirmed by experiments in closed systems. The first authors defined an equilibrium ratio $R = C_2 H_2/C_6 H_6$ function of P and T, which is relevant for further correlation to the type of deposited pyrocarbon (see Section 4).

2.3 Deposition mechanisms

It concerns essentially the condensation of gases on a solid surface, i.e. the nucleus and growing mechanisms. The basic thermodynamic approach for a hemispheric germ indicates that the Gibbs enthalpy for heterogeneous nucleation is always lower than for the homogeneous one, depending on the contact angle and the wetting conditions on a given substrate (Adamson, 1976).

The experimental consequence is that a pyrocarbon should be deposited at a lower T and (or) P than predicted by the classical homogeneous nucleation which gives rise to the formation of carbon blacks (Donnet and Voet, 1976). This is an interfacial property depending on both the nature of the gas phase and the solid surface. It has been shown that the substrate plays a role for the first pyrocarbon layers from the physical (roughness, curvature and surface energy) and chemical (nucleation sites) point of view. In particular it has been demonstrated that the active sites on a graphene surface and the plane edges are the preferential nucleation sites which control the first step for the kinetic deposition (Hoffman *et al.*, 1985). In this chemisorption process the main parameter is the active surface area (ASA) and its percentage with the total area (Ismail and Hoffman, 1991). More recently it has been evidenced by scanning tunneling microscopy (STM) on a pyrographite that the initial deposit is sensitive to the residence time parameter and a sort of wetting transition is detected associated with a morphological change indicating the influence of the gas composition on the adsorption process (Bouchard et al., 2001). This ideal substrate which presents a low surface energy is strongly modified for non-crystalline carbons as fibers; the density of active sites is much more higher and controls the pyrocarbon deposit (Ismail and Hoffman, 1991) and therefore the interfacial strength between fibers and matrix.

Other planar substrates have been used for electron microscopy works as, for example, alumina (Desprez and Oberlin, 1997; Soutric, 1998) or boron nitride (De Pauw *et al.*, 2003); apparently it does not change strongly the kinetics on the growing process after deposit of the first layers. This growing process has also been examined by several authors (Kaae, 1985). Two types of cone structures are usually recognized when the nucleus are created only on the substrate or regenerated at different levels (Diefendorf, 1960). These various features include the structure of nodules under different substrate conditions as presented in Fig. 5.2 (Coffin, 1964). As developed in classical CVD models (Bryant, 1977) the morphology of pyrocarbons with their cone growing structure, and through their density and porosity, are functions of the deposit conditions. In particular when the coating temperature is as high as 1,500 °C a less dense pyrocarbon is obtained which is considered as a non-graphitable carbon (Ford and Bilsby, 1976).

2.4 Comparison between standard CVD and CVI processes

In a standard technique, i.e. under isothermal and isobaric conditions the main difference between CVD and CVI concerns the type of substrate. As pointed out during the early studies (Kotlensky, 1973) there are very strong similarities between the pyrocarbon deposition



Figure 5.2 Cross sections of a nodule of pyrocarbon with the associated model (from Coffin, 1964): (a) nodule formed from surface asperity; (b) nodule formed from a foreign particle.

on a static substrate or a dynamic bulk surface, the so-called usual fluid bed technique, and the carbon growth inside a porous substrate. The phenomenological competition between the mass and heat transport phenomena and the overall chemical reactions is the basic point to consider. We can enounce two statements which are fundamental in this presentation:

(i) The overall chemistry by itself is mainly related to the local conditions in particular for the surface reactions. For a given precursor, they are supposed very similar in the gas phase for both CVD and CVI processes. However with porous preforms an increase of the surface to volume ratio (S/V) is a novel parameter to take into account (Hüttinger, 1998). As shown on the simplified schema presented Fig. 5.1, the deposits will result from the competition between the rate constants of the homogeneous and heterogeneous reactions.

(ii) The transport phenomena related to the hydrodynamics of fluids and to the energetic supply would be quite different. They are submitted to different scale factors related to the piece and reactor sizes which are sometimes very different (as in classical CVD) or comparable: they have to be examined for each type of process (see Section 3); on a general way the kinetic deposition of pyrocarbons can be represented by an Arrhenius plot which describes the general heterogeneous reactions of gases with porous solids (Hedden and Wicke, 1957). As presented in Fig. 5.3 three different regimes are recognized; they are related by a different rate limiting step. In regime I, at low temperatures the deposition rate (k) is



Figure 5.3 Characteristic Arrhenius plot: k versus T^{-1} with $k = k_0 \cdot \exp(-\text{Ea}/kT)$, involving a reacting gas and a porous medium (from Hedden and Wicke, 1957).

determined by the kinetics of the chemical reactions with an apparent activation energy (Ea) and the concentration gradient across the porous solid is negligible. At intermediary temperatures, within regime II the mass diffusion through the pores influences the rate of conversion which should correspond to about half-value of Ea. When the temperature is raised the diffusion factor becomes comparable with the rate reactions leading to an internal concentration gradient. Then in regime III at high temperatures the rate deposition becomes almost independant; the diffusion of gases through the stagnant boundary layer which always exists in a laminar flow (Carlsson, 1985), controls the process. In this last case the carbon infiltration inside the pores is not effective; a deposition rate of about a few microns per hour is usually observed. This is the main limitation for the usual making of these C/C composites as we will consider it in the following sections.

3 CVI processes and efficiency

The infiltration and the deposition of pyrocarbons in different porous substrates have been largely investigated starting from the classical isothermal and isobaric process. Its major drawback is the very low infiltration rate related to the diffusion constants. Many developments have been published to improve this situation in this multiparameter technique. As presented in Fig. 5.4, for the system responses we will analyze the matrix characteristics in relation with the following two major requirements, infiltration homogeneity and microstructure control of the matrix.

3.1 The process parameters

The numerous external constraints acting at different scales are divided into three different classes as summarized in Fig. 5.4:

(i) Geometrical and Energetical – considering the sources of heat and their distribution inside the reactor and the preform. The heating method, resistive inductive or radiative, is associated with either hot wall or cold wall reactors. This is a basic difference which



Figure 5.4 Summary of the parameters and system responses in CVI processes.

involves for hot wall technique isothermal and isobaric conditions whereas thermal gradients (Lieberman *et al.*, 1975) or pressure gradients and forced flows (Lackey and Starr, 1991) exist in the cold wall approach. This one can be also combined with either laser or DC and RF plasma uses (Lachter *et al.*, 1985; Levesque *et al.*, 1989).

The preform to densify is also crucial through its nature, orientation, and volumic fraction of the carbon fibers (Delhaès *et al.*, 1984); its position and volume occupation inside the furnace are noteworthy.

(ii) Hydrodynamical – the flow regime inside the reactor is related to the nature of the precursor fluid but also the size and the shape of the reactor; usually a low value of the Rayleigh number characterizes this laminar flow. The precursors are in a gaseous phase at different pressures; under isothermal conditions a laminar flow is expected and the residence time (see definition, Fig. 5.4) is the key parameter. However a forced flow will conduct to a quite different behavior as already demonstrated (Vaidyaraman *et al.*, 1996).

(iii) Chemical – the nature of the precursor is important even if the generic reactions are recognized (Fig. 5.1). For example natural gas i.e. methane, is the most stable hydrocarbon and the associated decomposition conditions will be specific compared to the other precursors. Besides liquid precursors, as cyclohexane and aromatic derivatives have been also used in a new fast densification technique that we will describe later (David *et al.*, 1995).

A complementary approach concerns the system responses as presented in Fig 5.3: the first ones are the material requirements, essentially the type of carbon matrix, the deposition rates, and the overall carbon yield. Its quality has to be optimized with the highest final density and a well defined type of microstructure. The classical "black box" approach which concerns only ex situ relevant parameters (Loll *et al.*, 1977) has been recently improved. Both experimental and theoretical approaches have been developed. In situ observations by FTIR in-line mass spectroscopy or gas chromatography, have deepened the gas chemistry (Chen and Back, 1979; Ferron *et al.*, 1999) and global modeling of engineering techniques are in constant progress (Ofori and Sotirchos, 1997). They will contribute in the future to the overall process control.



Figure 5.5 Sketches of the basic infiltration techniques (adapted from Kotlensky, 1973).

3.2 Outline of the principal methods

The basic infiltration techniques are schematically drawn in Fig. 5.5. As recently underlined by Golecki the various infiltration methods are at different stages of maturity and understanding (Golecki, 1997). The isothermal and isobaric CVI, the oldest "hot wall" technique, is still widely used both in laboratories and industry. Its main advantage is a good parameter control, in particular for large furnaces where a large number of complex preforms can be densified together. As already indicated a good matrix quality with a selected microstructure and a low residual porosity is obtained (Lackey and Starr, 1991). The main drawback is a quite long processing time, sometimes larger than 500 h with a very slow rate of deposit associated with a very low overall precursor efficiency, a few percent only with the natural gas. New routes to develop rapid infiltration techniques have been explored to increase the process efficiency. We present them, giving some interesting examples:

(i) Derived from the isothermal process, three ways have been explored: the catalytic CVI using transition metals for increasing the rate deposition (McAllister and Wolf, 1993), the plasma enhanced CVI (Levesque *et al.*, 1989), and the pulsed flow where a cyclic evacuation of the reaction chamber and a back filling with reagents is done (Dupel *et al.*, 1994). These approaches appear more interesting for the basic understanding of the infiltration mechanisms than to get an economical and technical gain.

(ii) Pressure gradient and forced flows: Several reactors have been built to control the gas hydrodynamics under isothermal conditions or with thermal gradient (Lackey and Starr, 1991). In particular the forced flow-thermal gradient CVI process (see Fig. 5.6) has been thoroughly developed (Vaidyaraman *et al.*, 1995). The fabrication of valuable C/C composites with a matrix of uniform high thermal conductivity onto conventional size fibers is realized in a few hours under controlled parameters (Lewis *et al.*, 1997).

(iii) Strong thermal gradients under quasi isobaric conditions: this is the case of cold wall reactors with a graphite susceptor inside (see Fig. 5.5d). The precursors are in a gaseous or liquid state: nevertheless in both situations there is a mobile reacting front on which the vapors decompose to produce the carbon deposit. Two main type of reactors have been realized with similar cylindrical geometries, the rapid vapor phase densification and the film boiling technique based on a liquid reservoir (Fig. 5.7). Both techniques are very efficient, a single cycle of densification for a few hours as for the forced flow method is sufficient in the range. A high conversion efficiency is obtained, one order of magnitude higher than is classical processes i.e 20-50%, associated with a good quality of the final products (Golecki et al., 1995). To get a better insight on this type of process a small laboratory reactor equipped with an internal resistive heater has been built up (Rovillain et al., 2001) which can work with various liquid precursors. As shown in Fig. 5.8 this process is based on a mobile reactive front with a steep densification profile which starts from the central part of the preform to the outside. This novel process has been widely investigated these last years concerning the chemical influence with halogen derivatives or iron catalytic effect (Okuno et al., 2001) and the hydrodynamical aspect with a mass barrier effect and the influence of high pressure reagents (Beaugrand, 2000). The essential parameter appears to be the evolutive thermal gradient across the preform which controls both the high infiltration speed and the type of pyrocarbons.

To conclude it should be mentioned that these industrial applications are covered by numerous patents; a comparison between these processes with their advantages and disadvantages are presented in Chapter 6 (Golecki, 2003).



Figure 5.6 Schematic of the preform and the reactor used in forced-CVI process (from Lewis *et al.*, 1996).



Figure 5.7 Boiling film CVI reactor with induction heating of an internal graphite susceptor immersed in the liquid precursor (from David *et al.*, 1995).

4 Pyrocarbon microstructures

For a long time different types of deposited pyrocarbons have been recognized and well characterized at various length scales. These microstructures are on the one hand dependant on the experimental parameters and techniques and on the other they present reproducible structural and physical characteristics that we will summarize. Indeed it has been observed that typical intrinsic microstructures which are obtained are basically the same for every CVD and CVI process. We will discuss both aspects in the following section.

4.1 The different types of pyrocarbons

In a pioneering work Bokros has identified the experimental conditions favoring the depositions in fluid beds of anisotropic types, i.e. laminar or granular-columnar, and isotropic carbon structures (Bokros, 1969). Following Bokros' work, Lieberman and Pierson in the



Figure 5.8 Boiling film technique (from Rovillain *et al.*, 2001): (a) Laboratory reactor with resistive heating; (b) cross-section observed by optical microscopy of a partially densified felt (with cyclohexane at T = 1250 °C during 30 min); (c) radial densification profile determined from the photograph presented in (b).

1970s, have proposed a structural classification issued from this optical microscopy observations for the densification process of porous substrates. From polarized optical analysis they defined three main microstructures. They are called smooth laminar (SL), rough laminar (RL), and isotropic (ISO) carbons respectively, based on the shape and contrast of the optical photomicrographs of carbon composites; intermediary state between smooth laminar and isotropic microstructure is also noticed as granular or dark laminar carbon (Lieberman and Pierson, 1974). We will define these structural organizations at different complementary scales, thanks to X-ray diffraction, optical, and electronic microscopies respectively.

The optical texture of these pyrocarbons has been defined from the bireflectance of graphite and graphitic carbons. Several methods have been proposed to quantify the reflectance anisotropy (Bourrat *et al.*, 2000). One usual way is to measure the extinction angle Ae between cross polarizer and analyzer set up perpendicularly to a coated fiber because an axial symmetry is required to observe the Maltese cross. This angle depends on the amplitude of the beam transmitted parallel to the anisotropic plane regarding the normal direction. As presented in Table 5.1 the larger the extinction angle, the higher is the structural anisotropy (the intermediary dark laminar structure is defined for $4^{\circ} < Ae < 12^{\circ}$).

A complementary approach is to measure the layer anisotropy by electron diffraction by means of a varieties of transmission electron microscopy techniques (TEM) (Bourrat et al., 2000). The different pyrocarbons are described by the size of the basic structural units (BSU), the mean carbon layers (L2), and the number of these aromatic layers coherently stacked together with a characteristic interlayer distance (d_{002} spacing) and defined with a mean orientation angle. Moreover recent TEM observations have shown that the growing modes are different with a dense columnar type for RL microstructure and a rather nonplanar lateral type for SL one (Lavenac, 2000). As summarized in Table 5.1 every microstructure is defined through specific structural and physical properties. The most anisotropic microstructure is RL which presents also the largest specific mass because of both the better nanostructural organization and the absence of any intrinsic porosity as observed by TEM (Goma and Oberlin, 1986). The most significant point is that RL is the only one which is graphitable under further heat treatment (HTT °C), i.e. evoluting toward the stable thermodynamic phase of hexagonal graphite as indicated by the d_{002} spacing in Table 5.1 (for a single crystal of graphite $d_{002} = 3.354$ Å at room temperature). Following the same way the electronic, thermal, and mechanical characteristics of each microstructure has been recognized for a long time (Granoff et al., 1973; Loll et al., 1977). They are in favor of the RL microstructure for most of the composite applications. A bulk property as the diamagnetic susceptibility and its anisotropy can be used to relate the preferred orientation of the surface delocalization of π electrons. As in optical birefringence the Landau type diamagnetism depends on the aromatic size, the L2 parameter, and the associated orientation angle (Flandrois, 2000). A relationship exists between this normalized diamagnetic anisotropy and the matrix density as shown in Fig. 5.9 (Delhaès, 1998), and in agreement

Pyrocarbon microstructure Structural and physical characteristics	Isotropic (ISO)	Smooth laminar (SL)	Rough laminar (RL)
Optical anisotropy	$Ae < 4^{\circ}$	$12^{\circ} < Ae < 18^{\circ}$	$Ae > 18^{\circ}$
Extinction angle: Ae	dark image	smooth crosses	irregular black crosses
Diamagnetic anisotropy	very weak	weak	strong
TEM experiments	micropores	flattened pores	no pores
Graphitizability	No	No	Yes
d_{002} after HTT = 2800 °C	~ 3.44 Å	<3.44 Å	≡3.37 Å

Table 5.1 Physical and structural characteristics of the main carbon microstructures (from Delhaès, 1998)



Figure 5.9 Relationship between the relative diamagnetic anisotropy $\Delta X \%$ and the matrix density for each type of microstructure (from Delhaès, 1998).

with recent TEM observations. Besides the related mean values, upper for the isotropic microstructure than for the anisotropic one, indicates more developed BSU as expected for a longer residence time in gas phase (Fig. 5.1).

These results are confirmed by Raman spectroscopy; indeed in first order Raman spectra, the ideal graphite presents a characteristic single peak at 1580 cm^{-1} (G-band) but for any type of graphitic carbon, a second peak is appearing around 1350 cm^{-1} (D-band) (Lespade *et al.*, 1984). The intensity ratio between these two bands, as already proposed (Truinstra and Koenig, 1970), is a valuable indicator to characterize the local organization occurring in these microstructures. A characteristic behavior is observed for these microstructures which behave as a regular metastable phase with intrinsic characteristics which are not process dependent.

4.2 Existence diagram and phase stability

A correlation between the deposition parameters and the defined microstructures can be drawn for a given experimental set-up working under isothermal and isobaric conditions



Figure 5.10 Existence diagram of the different microstructures obtained by infiltration inside a carbon felt and playing with two parameters, the proportion of CH_4 in CH_4-N_2 mixture under atmospheric pressure and the temperature of deposition (from Loll *et al.*, 1977).

(hot wall reactors). Indeed an existence diagram which represents the different "phases" can be drawn for a given set of experimental constraints. As presented Fig. 5.10 a general boundary is defined between homogeneous vapor nucleation and heterogeneous one at the gas–solid interface resulting from the competing homogeneous and heterogeneous chemical reaction (see Fig. 5.1). Then for a given set of hydrodynamic parameters, in particular for a fixed gas flow, it is shown that SL is formed at low temperatures and high partial pressure of methane whereas RL is deposited in the medium range and ISO at high temperature with a rather low pressure. The boundary between RL and SL domains is sharp, reminiscent of a first order phase transition, but the change between SL and ISO microstructures is progressive, justifying the introduction of a granular or dark laminar intermediate.

These observations are functions of the experimental parameters as the nature and the initial porosity of the substrate (Delhaès *et al.*, 1984) or the nature of the hydrocarbon precursor (Ferron *et al.*, 1999). As shown in Fig. 5.10 a sequence SL–RL–SL is observed when the residence time is increasing at a fixed deposit temperature. More generally they do not depend on the used process as for example with the film boiling technique where RL microstructure is preferentially deposited (Bruneton *et al.*, 1997).

Besides, a combination of alternative microstructures is quite often detected during the overall infiltration process in particular inside a bundle of single filaments (Pierson and Lieberman, 1975; Loll *et al.*, 1977; McAllister and Wolf, 1993; Dupel *et al.*, 1994; Benzinger and Hüttinger, 1999b). Sequences of (RL–SL) microstructures are observed by polarized optical microscopy which could result from a change of the local conditions, out of the control of the external parameters. These morphological changes are tentatively interpreted as a bi-stability effect known in non-linear thermodynamics systems (Vignoles *et al.*, 2001).

4.3 Deposition and infiltration rates

These process characteristics are strongly dependent on the selected reactor but some global trends can be drawn.

(i) The deposition rate defined as the thickness or locally deposited pyrocarbon per unit of time, on a planar or curved, as a single filament, substrate. It is well known that for the CVI isothermal process because of the rate limiting step due to the diffusion factor (see Fig. 5.1) a very low deposition speed $(0.1-0.2 \,\mu m \, h^{-1})$ is recorded.

Using the so-called "cold wall" reactors an increase of these deposition rates is obtained. For example, in the case of forced CVI values about $3 \,\mu m h^{-1}$ with propylene as precursor are measured (Vaidyaraman *et al.*, 1996). In presence of thermal gradients with either gas or liquid precursors, higher values are reached up to $50 \,\mu m h^{-1}$ in the case of the boiling technique with a very reactive hydrocarbon (Rovillain *et al.*, 2001) these deposition rates measured under controlled conditions can be related to the apparent activation energy (Ea) and the associated chemical. Indeed it has been shown (Ferron *et al.*, 1999). That the observed structural transitions are related with a kinetic regime change as presented in Fig. 5.11. In the literature many (Ea) values are found which are more or less dependant on the experimental conditions and difficult to compare directly. In the present case however this significant change is attributed to a different mechanism involving interfacial effects (Lavenac, 2000).

(ii) The infiltration rate related to the kinetic of mass uptake which is the primary response examined by almost all the authors. In most of the cases a first order type reaction is used to fit these data (Palmer and Cullis, 1965); one example of comparative study with different porous substrates under constant temperature (Marinkovic and Dimitrijevic, 1985) has shown that the infiltration rate is determined by the open pore volume rather than the total surface area. This result means the homogeneous reactions are more efficient than the heterogeneous ones on the pore walls. One way to get a deeper insight on the infiltration mechanism is to work with model pores of various diameters and lengths. After some earlier attempts (Bickerdike *et al.*, 1961), two recent works have led to interesting results. First, Dupel *et al.* (1994) have used straight pores with rectangular cross-sections (widths: $60-320 \,\mu$ m) under pulsed CVI conditions. The deposits present both a thickness and



Figure 5.11 Plot of the deposition temperature versus the residence time under isobaric conditions, furnishing the existence diagram with the microstructure domains and the associated activation energies expressed in kJ mol⁻¹ (from Feron *et al.*, 1999).

a texture profile, as shown in Fig. 5.12 for a selected range of parameters (Dupel, 1993). For different residence times with an increasing depth inside the pore we observe a decrease of thickness and a change of microstructure. At the pore entrance a RL microstructure is detected which is changed in SL type at a deeper level. As indicated by the authors this is the signature of a local change in the deposition mechanism. Secondly, Hu *et al.* (2000) carried out similar experiments with different circular pores. In particular for a given capillary (1 mm in diameter and 17 mm in length) with low pressure methane decomposed at 1,100 °C they show an increase of the deposition rate from the mouth to the depth of the pores. This opposite result dependant also of the residence time is explained by the competition between heterogeneous and homogeneous reactions and the control of the A/V ratio (see Fig. 5.1).

At the contrary the reaction–diffusion competition is not so critical in the presence of a T or P gradient. The infiltration rate is governed by the displacement of the reacting front inside the porous subtrate (see Section 5). It has been established for the film boiling technique that a relation exists between the deposition on a single filament and the bulk infiltration rate with a proper account of the thermal gradient (Rovillain *et al.*, 2001) (Fig. 5.7).

(iii) Comments about the mechanisms-microstructures relationship in hot walls reactors. Two points are relevant concerning both the hydrodynamic and the chemistry. The hydrodynamic



Figure 5.12 Pyrocarbon infiltration with the associated deposit thickness (a) and the optical anisotropy coefficient Ae (b) along a 60 μ m model pore, as a function of the pore depth and for different residence times (r); the experimental conditions are T = 1,050 °C, P = 1kPa and propane used as pristine gas (adapted from Dupel, 1993).

flow is characterized by the residence time (Fig. 5.4) which is defined in a free space for a laminar flow in piston mode. This parameter is neither concerned by the chemical reactions nor the transport in porous media. The so-called maturation influence for homogeneous reactions (Marinkovic and Dimitrijevic, 1985; Dupel *et al.*, 1994) is valid as long as the furnace reacting volume is large compared to the preform one and the associated residence time is a valuable parameter. Inside a porous substrate characterized by the ratio A/V, and its apparent density the situation is quite different. When it constitutes a large volumic fraction of the reaction (Hüttinger, 1998) the residence time definition is not so straightforward.

For the chemistry it seems that in some cases the increase of ratio $R = (C_2H_2/C_6H_6)$ established for thermodynamic equilibrium (Lieberman and Pierson, 1974), is related to the observed microstructure sequence, i.e. SL–RL–I (Benzinger and Hüttinger, 1999a,b). However this is not in disagreement with other series of results (Ferron *et al.*, 1999; Lavenac, 2000; Bouchard *et al.*, 2001) for which SL type deposit is related to a majority of aliphatics and RL one mainly to aromatics (note that in presence of polyaromatics after maturation, the isotropic phase is supposed to be deposited in agreement with the magnetic measurements already discussed in Section 4.1). To get a better understanding, the detection of the more active species, in particular the free radicals, at the interface is obligatory and is the control of their chemical gradients inside the pores which has to be determined for a better insight. The last remark concerns the observed morphological changes during a given infiltration which indicates a coupling effect between the hydrodynamic and chemical effects (De Pauw *et al.*, 2003).

5 Physical models

All the reactors are open thermodynamic systems with matter and heat exchanges; their overall balance controls both the deposition rate on a substrate and the infiltration mechanism inside a porous preform. Several models have been developed at different levels of complexity to understand these processes that we will present in relationship with the experiments. For clarity it is still useful to distinguish between the isothermal–isobaric reactors and those working under a strong thermal gradient, alternatively with either forced or pulsed flows.

5.1 Isothermal "hot wall" reactors

In CVD technique a large volume reactor is used where a laminar flow in a free medium is expected for the gases. As it has been demonstrated the film growth rate on a flat surface is dependent on the slower mechanism of either the molecular diffusion or the surface reactivity. It has been shown (Van Den Brekel and Bloem, 1977) that the deposition state is characterized by a dimensionless number which is for example the Sherwood number:

$$N_{\rm sh} = k \cdot d/D \tag{1}$$

where k is the kinetic constant for mass deposition, D is the molecular diffusion constant, usually considered to be Fickian (D = -grad C, where C is the molecular concentration), and d is a characteristic distance, e.g. the boundary layer thickness in the gas phase (Carlsson, 1985) which is extrapolated to a typical length in the case of a porous substrate with defined pore sizes.

In classical CVD the situation is described by defining $N_{\rm sh} < 1$, this is the mass transport regime presented in Fig. 5.2 which allows also a homogeneous deposition inside the pores. Besides morphological instabilities are associated with this competition; in particular a realistic model for controlling growth conditions has been proposed (Bales *et al.*, 1989). Introducing also mass transport along the surface driven by capillary forces, this kind of model leads to different morphologies as for example observed on ramified amorphous filaments of carbon (Banhart, 1997). This approach is reminiscent of the different type of microstructures which are observed both by CVD and CVI techniques (see Section 4.2) even if no clear comparison could be drawn so far.

Concerning CVI, the modeling analysis is more complex and one of the simplest but efficient model is issued from Thiele's work (Thiele, 1939) used initially for heterogeneous catalysis problems. It is assumed that the pores are independent and cylindrical with a given diameter, and the chemical reaction giving rise to the carbon formation is of the first order. The overall process is defined through a dimensionless number called Thiele modulus:

$$\phi \alpha (k/d)^{1/2} \tag{2}$$

which is analogous to the square root of $N_{\rm sh}$.

The efficiency of the process is defined by the infiltration factor inside a pore $(\eta = t \operatorname{gh} \phi/\phi)$ as already defined (Fitzer and Hegen, 1979) which can be compared with the experimental results using pore models. To ameliorate the infiltration rate it is possible to increase the chemical reactivity by plasma enhanced CVI for example but a strong deposit gradient is observed (Levesque *et al.*, 1989), which corresponds to a regime change when $\phi \approx 1$. A 3D percolation model where the connectivity between pores whithout any tortuosity factor is taken into account to explain this result (Delhaès, 1998). The infiltration is controlled, in absence of any effective convection, by the diffusion processes which are not only the classical Fick term but also the Knudsen one which introduces the collisions with the solid surfaces. Usually the Knudsen number is indicating the predominant term:

$$K_n = \lambda/d \tag{3}$$

where λ is the molecular mean-free path for a given molecule (from Fick and Knudsen terms) and *d* the characteristic length is the mean pore diameter which is progressively reduced during the process. At a given stage K_n is lower than 1, the diffusion regime becomes ballistic and the carbon deposit can be affected by this effect which normally occurs is the nanometric range. This is an empirical approach because we are in presence of a multicomponant and evolutive system due to the complex chemistry; indeed the light species as hydrogen are playing a crucial role in such a confined space which is not fully elucidated.

To overcome all these difficulties it is necessary to develop a mathematical model which describes the dynamic behavior of isothermal CVI: the so-called dusty gas model (Sortichos, 1991). The equations for momentum, heat, and mass balances of the whole process including the interfacial hydrodynamic problems, a simplified chemical path, the multicomponent diffusion, and the tortuosity factor for the porous substrate have to be established. A few theoretical works have attempted to solve this difficult problem (McAllister and Wolf, 1993; Vignoles *et al.*, 2001) which are out of the scope of this chapter.

5.2 Non-isothermal or (non-isobaric) conditions: "cold wall" reactors

As has been described in Section 3.2 temperature or pressure gradient generally results in shorter process time than isothermal operation. This is due to the existence of a gradient field which enhances the driving force associated with the thermal and mass transports from the cold face to the hot one inside the preform (Bristow and Hill, 1975). A spatial separation between the chemistry and the transport zones results with the existence of a mobile reacting front. This is a new class of phenomenon that we introduce in a first approach before discussing about the mechanisms which are involved in the presence of a steep thermal gradient.

(i) *The related phenomena* This class of non equilibrium systems is defined when a pressure or thermal front is associated with interfacial chemical reactions. Such a situation is encountered for example when a shock wave is created for making artificial diamonds but most of the cases are related to thermal effects. A drastic thermal front exists for the degradation of carbon materials by oxidation or by ablation effects occuring in spacecraft aero-dynamic during the atmospheric re-entry or in gaseous combustion including the models of flame front (Clavin and Linan, 1984). Another similar system is the dynamics of a frontal polymerization associated with exothermic reactions (Posman *et al.*, 1998). Their common point is a coupling effect between the chemistry and the hydrodynamics which is delicate to handle theoretically.

(ii) *Fast densification processes* The film boiling chemical vapour infiltration technique has been mainly investigated by either inductive (Bruneton *et al.*, 1997) or resistive heating (Rovillain *et al.*, 2001) but strong similarities exist with other thermal gradiant furnaces working with gas precursors (Golecki *et al.*, 1995). A comparison between the experimental situations with a combustion front in the case of a subsonic premixed flame



Figure 5.13 Process modelization for the film boiling technique: sketch of the temperature radial profile for a bench reactor with the main different functionalized parts (Rovillain *et al.*, 2001).

has been proposed (Rovillain *et al.*, 2001). This model leads to a process analysis presented in Fig. 5.13 starting from the center, where the resistance heater is located. The temperature profile of the radial section of the reactor can be divided into five parts. As shown on the drawing each of them is characterized by a specific function:

- Part I is the graphite heater and the already densified preform. This is the heat source controlled at a constant temperature T and the heat transfer is due to the thermal conduction of the composite.
- Part II, the reacting front characterized by a deposition thickness and a large thermal gradient. All the chemical reactions are confined inside this narrow space so possibly described from flame theory.
- Part III, the porous preform where the complex heat and mass exchanges are located. The heat transfer inside this multiphasic system is due to the solid thermal conduction, to the diffusion–convection mechanism of the gases and the radiation effects. The mass transfer is related with the respective molecular gradient (Fick law) and eventually with the temperature gradient (Soret effect).
- Part IV, the felt external portion where the precursor is boiling and the liquid and gas phases coexist; the calefaction effect is observed inside this biphasic regime.
- Part V, outside the preform, the precursor is boiling at a constant temperature: this is the mass reservoir for carbon deposit.

From the experimental deposition rates on each fiber and the associated front propagation rate inside the preform (Rovillain *et al.*, 2001) which can reach 2–3 mm per hour an estimation of the mass transport coefficient is possible. In steady-state conditions it is possible to calculate from the classical diffusion equation for an ideal binary mixture (e.g. cyclohexane and hydrogen) the Fick coefficient which is about the correct order of magnitude. It means this is apparently the main driving force; the effect due to the steep thermal gradient and the influence of the porosity (Knudsen term) are not crucial, at least with a felt used as a light preform (apparent density: 0.1). In any case a complete modeling of these CVI processes with resistive or inductive heating is the next work to accomplish for a better insight and efficiency. It turns out that by comparison with the other related phenomena, the interaction between chemistry and hydrodynamics has to be taken in account to develop a valuable model for infiltration.

6 Carbon-carbon composites

The current purpose is not to fully describe their applications but rather their intrinsic characteristics together with the associated interfacial properties which are dependent of the type and the nature of used preforms. For the industrial uses we will just mention selected examples which emphasize their peculiar properties.

6.1 Composite quality

Two types of requirements have to be considered, the matrix quality by itself and the associated interfacial behavior. The type of microstructure, with its bulk density which is related to the voids, residual porosity and cracks, is first examined. The rough laminar (RL) pyrocarbon is usually searched because of its good thermal and mechanical characteristics associated to the higher grain density and graphitability (see Section 4.1). Therefore the type of process for a selected preform is of primary importance to get a stable and robust RL "phase" with a low residual porosity (Granoff *et al.*, 1973; Delhaès *et al.*, 1984). A complementary characteristic is the high temperature behavior, high thermo-mechanical properties stay up to 2,000 °C except under oxidizing atmosphere. To increase the oxidation resistance of carbons several approaches have been done. One is to dope the matrix to boron which modifies the microstructure and induces an inhibition mechanism against the oxidation (Jacques *et al.*, 1996). An alternative way is to protect the pyrocarbon with a ceramic coating as, for example, silicon carbide (Bines, 1993).

Indeed the type of carbon fiber and its surface characteristics control the composite behavior:

(i) Choice of the space distribution: the different fiber bundle arrays are characterized by their dimensionality as felts, unidirectional bundles, weave patterns, and tri- or multidirectional arrays. The fiber volume fraction is increasing with the arrays dimensionality and the mean pore size is decreasing giving rise to changes in the infiltration process.

(ii) Control of the fiber surface: its choice, rayonne, PAN, or mesophase based and a preliminary treatment will give rise to different works of adhesion which depend on the surface energy as for the wettability characteristics (Vix and Ehrburger, 2003). The shape, curvature, and roughness of the fiber as also its graphene surface with the presence of nucleation sites are influent for the type of physical or chemical interactions. Following this difficult analysis the sort of dry (plasma) or wet treament (chemical or electrochemical attack) can radically change its behavior (Manocha *et al.*, 1989). The type of deposited pyrocarbon will be controlled as for example when an interphase is introduced to improve the mechanical properties in a unidirectional model composite (Naslain *et al.*, 1999).

The mechanical applications are based on the transfer of fiber properties to the matrix which depends on different mechanisms as just discussed above and including the residual thermal stress due to the anisotropy of the thermal expansion coefficient. A compromise between strong and weak bonding at the interface is necessary to optimize the efficiency and the fracture toughness; ultimately a catastrophic type of failure with a brittle behavior is observed but by making use of the fiber surface treatment a pseudo plastic failure mode is



Figure 5.14 Schematic mechanical properties with a strain–stress plot of unidirectional (1D), bidirectional (2D) and tridirectional (3D) composites (from Fitzer, 1987).

obtained. One generic example is presented in Fig. 5.14 where the effect of the bundle orientation on the tensile strength is presented (Fitzer, 1987). When the strain is applied in the bundle directions the 3D composites exhibits a lower but isotropic value accompanied with a pseudo-plastic behavior (McEnaney and Mays, 1993).

Other examples have been published relative to standard flexural tests when the type of deposited microstructure is controlled (Kimura *et al.*, 1981; Delhaès *et al.*, 1984; Oh and Lee, 1989). The influence of the matrix concerning the bending strength and the associated modulus have been recognized in particular for weave preforms.

6.2 Applications overview

The carbon–carbon composites are used for different applications where combined properties are always involved. We summarize three of them (Fitzer, 1987) illustrating valuable examples.

(i) Heat shields of space reentry vehicles and thermo-mechanical properties. A figure of merit for thermal shocks and ablation can be defined as the high thermal stress resistance (TSR) (Lieberman *et al.*, 1975):

$$TSR = \sigma \cdot K/E \cdot \Delta \tag{4}$$

where σ is the tensile stress, K the thermal conductivity, E the Young's modulus, and Δ the linear thermal expansion coefficient.

As pointed out (Thomas, 1993) this coefficient is very high in C/C composites compared to standard alloys and still valuable at elevated temperatures up to 2,000 °C.

(ii) Brakes for aircrafts and terrestrial vehicles (race cars, trucks, and fast trains); tribological properties are involved combining surface and bulk characteristics. The graphitic carbons present a low coefficient of friction which is used for many applications involving mobile pieces. For brakes the frictional behaviour is associated with its ability to absorb and conduct away large quantity of heat. In presence of different atmospheres complex physico-chemical interactions are superimposed to the mechanical ones. This mixed effect is explained by the role of surface debris forming the third body composed of fine powder involved in the sliding speed; the resulting wear and associated efficiency are explained with the presence of this transfer film (Diss and Brendle, 1997). It is interesting to quote that this situation is similar to those described for depositive phenomena exhibiting a steep thermal gradient (see Section 5.2).

(iii) Biocomposites for prostheses and implants: the carbon presents the best biocompatibility with blood, tissues, and bones. This can be associated with adapted mechanical characteristics for ankles and knee prostheses or plates in ostheosynthesis (Fitzer, 1987). In the recent years, however, these chirurgical applications have not been actively developed because other ceramics or alloys are currently employed.

7 Conclusion and outlook

Our approach is based on the relationship between processes and materials. On one hand the process analysis concerns both the principles and the techniques, i.e. a comparison between the different types of reactors (Sections 2 and 3). On the other hand the deposited pyrocarbons where the established structure–property correlations have been presented; it leads to

reproducible type of microstructures necessary for the applications including high temperature behavior and graphitation (Sections 4 and 6). Finally the logical link between them is through the physical models which should explain the whole process if all the chemical, thermal, and hydrodynamical components are included (Section 5). In particular it will be necessary to define a minimum set of indispensable reactants to modelize correctly the overall chemistry.

The formation mechanisms in confined media are rather complex but a general description is given which covers from the deposition on a bulk surface to the soot nucleation in the gas phase. It appears that a better knowledge of the interfacial physics and chemistry is necessary for both the deposition mechanism and the resulting composite characteristics. Coupled with the development of local sensors to measure the effective constraints it turns out that the observed morphological instabilities could be analyzed and controlled.

As noticed before, these CVI processes are characterized by different scale factors and also by different time scales. Indeed the surface reactions are usually fast with a characteristic time about a microsecond, the residence time in the gas phase is the range of several seconds or more and the processing time is at least ten thousand times longer. For the industrial CVI reactors the main difficulty is to control both these different length and characteristic times for making the desired type of metastable phase of pyrocarbon (in general the RL microstructure) under robust experimental constraints to obtain an homogeneous bulk piece. This is one blocking point of development of the fast densification techniques that we have presented in this review.

In conclusion, the new pressure or thermal gradient reactors, as developed for the fast boiling technique, lead to a shorter processing time and an increased process efficiency which need to be extended to an industrial scale. An economical gain could be expected as long as the matrix quality and the interfacial interactions are optimized in these C/C composites.

References

Adamson, A. W. (1976). Physical chemistry of surfaces (Third edition, Wiley-interscience editor). Bales, G. S., Redfield, A. C., and Zangwill, A. (1989). Phys. Rev. Lett. **62**, 776–779.

Banhart, F. (1995). Phys. Rev. E 52, 5156-5162.

Beaugrand, C. (2000). PhD thesis, University of Orleans (France).

Benziger, W. and Hüttinger, K. J. (1999a). Carbon 37, 181-193.

Benziger, W. and Hüttinger, K. J. (1999b). Carbon 37, 1311-1322.

Bickerdike, R. L., Brown, A. R. G., Hugues, G., and Ranson, H. (1961). Fifth International Carbon Conference, 575–582.

Bines, E. B. (1993). In *Essentials of Carbon–Carbon Composites* (Ed. by C. R. Thomas, Royal Society of Chemistry), ch. 8, 204–227.

Bokros, J. C. (1969). Chemistry and Physics of Carbon (Ed. by P. L. Walker), Vol. 5, 1-118.

Bouchard, E., Lavenac, F., Roux, J.-C., Langlais, F., and Delhaès, P. (2001). Advanced materials-CVD 7, 125–130.

Bourrat, X., Trouvat, B., Limousin, G., Vignoles, G., and Doux, F. (2000). J. Mater. Res. 15, 92–101.

Bristow, H. A. S. and Hill, J. (1975). I. Chem. E. Symposium Series No. 43, 5/1-5/11.

Bruneton, E., Narcy, B., and Oberlin, A. (1997). Carbon 35, 1593–1598 and 1599–1611.

Bryant, W. A. (1997). J. Mater. Sc. 12, 1285–1300.

Carlsson, J. O. (1985). Thin solid films 130, 261-282.

Chen, C. J. and Back, M. H. (1979). Carbon 17, 175-180.

Clavin, P. and Linan, A. (1984). In *Non-equilibrium Cooperative Phenomena in Physics and Related Fields* (Ed. by M. G. Velard, NATO ASI series B) **116**, 291–338.

- Coffin, L. F. (1964). J. of Amer. Chem. Soc. 47, 473-478.
- David, P., Narcy, B., Lulewicz, J. D., Ravel, F., and Schulmann, S. (1995). Proceedings of ICCM-10, Vol. 4, 611–616.
- Delhaès, P. and Carmona, F. (1981). In *Chemistry and Physics of Carbon* (Ed. by P. L. Walker and P. A. Thrower) Vol. 17, 89–174.
- Delhaès, P., Trinquecoste, M., Pacault, A., Goma, J., Oberlin, A., and Thebault, J. (1984). J. de Chimie-Physique **81**, 809–817.
- Delhaès, P. (1998). Proceedings of Euro CVD-11 (Ed. by M. D. Allendorf and C. Bernard), part 4, 486–495.
- Delhaès, P. (2000). In *World of Carbon*, "Graphite and precursors" (Ed. by P. Delhaès, Gordon and Breach Science Publishers), Vol. 1, 1–24.
- Delmonte, J. (1981). *Technology of Carbon and Graphite Fiber Composites* (Van Nostrand Reinholt company, USA).
- De Pauw, V., Reznik, B., Kalhofer, S., Gerthsen, D., Hu, Z. J., and Hüttinger, K. J. (2003). Carbon 41, 71–77.
- Desprez, J.-F. and Oberlin, A. (1996). Tanso, 17, 2-12.
- Diefendorf, R. J. (1960). J. de Chimie-Physique 57, 815-821.
- Diefendorf, R. J. (1969). In *Reactivity of Solids* (Ed. by J. W. Mitchell, R. C. De Vries, R. W. Roberts, and P. Cannon) 471–473.
- Diss, P. and Brendle, M. (1997). Wear 203-204, 564-572.
- Donnet, J.-B. and Voet, A. (1976). Carbon Black (Ed. by M. Dekker).
- Dupel, P. (1993). PhD thesis, University of Bordeaux I (France).
- Dupel, P., Pailler, R., Bourrat, X., and Naslain, R. (1994). J. Mater. Sci. 29, 1056-1066.
- Ferron, O., Langlais, F., Naslain, R., and Thebault, J. (1999). Carbon 37, 1343-1353.
- Fitzer, E. and Hegen, D. (1979). Angew. Chem. Int. English Edition 18, 295-304.
- Fitzer, E. (1987). Carbon 25, 163-190.
- Flandrois, S. (2000). In *World of Carbon*, "Graphite and Precursors" (Ed. by P. Delhaès, Gordon and Breach Science Publishers), Vol. 1, ch. 4, 71–86.
- Ford, L. H. and Bilsby, C. F. (1976). J. of Nuclear Materials 60, 79-88.
- Frenklach, M. (1996). Twenty-sixth International Symposium on Combustion (Pittsburgh, USA), 2285–2293.
- Golecki, I., Morris, R. C., Narasimhan, D., and Clement, N. (1995). Appl. Phys. Lett. 66, 2334–2337.
- Golecki, I. (1997). Materials Science and Engineering R20, 37-124.
- Golecki, I. (2003). In *World of Carbon*, "Fibers and composites" (Ed. by P. Delhaès, Taylor and Francis), Vol. 2, ch. 6.
- Goma, J. and Oberlin, A. (1986). Carbon, 24, 135-142.
- Grisdale, R. O. (1953). J. of Applied Physics 24, 1082-1091.
- Granoff, B., Pierson, H. O., and Schister, D. N. (1973). J. Composite Materials 7, 36-52
- Hedden, K. and Wicke, E. (1957). Third Biennial Carbon Conference (Buffalo, USA), 249-256.
- Hoffman, W. P., Vastola, F. J., and Walker, P. L. (1985). Carbon 23, 151-161.
- Hu, Z. J., Schoch, G., and Huttinger, K. J. (2000). Carbon 38, 1059–1065.
- Hüttinger, K. J. (1998). Advanced Materials CVD 4, 151-158.
- Inagaki, M. (2000). New Carbons: Control of Structures and Functions (Ed. Elsevier).
- Ismail, M. K. I. and Hoffman, W. P. (1991). Carbon 29, 587-594.
- Jacques, S., Guette, A., Bourrat, X., Langlais, F., Guimon, C., and Labrugere, G. (1996). Carbon 34, 1135–1143.
- Kaae, J. L. (1985). Carbon 23, 665-673.
- Kimura, S., Yasuda, E., Takase, N., and Kasuya, S. (1981). High Temp. High Press. 13, 193–199.
- Kotlensky, W. V. (1973). In *Chemistry and Physics of Carbon* (Ed. by P. L. Walker and P. A. Thrower), Vol. 9, 173.
- Lachter, A., Trinquecoste, M., and Delhaès, P. (1985). Carbon 23, 111-116.

- Lackey, W. J. and Starr, T. L. (1991). In *Fiber Reinforced Ceramic Composites* (Noyes Publ. Park Ridge, USA), 397–449.
- Lavenac, J. (2000). PhD thesis, University of Bordeaux I (France).
- Lavenac, J., Langlais, F., Feron, O., and Naslain, R. (2001). Composites Science and Technology 61, 339–345.
- Lespade, P., Marchand, A., Couzi, M., and Cruège, F. (1984). Carbon 22, 375-385.
- Levesque, O., Ricci M., Trinquecoste, M., and Delhaès, P. (1989). J. de Physique C5 50, 269-279.
- Lewis, J. S., Lackey, W. J., and Vaidyaraman, S. (1997). Carbon 35, 103-112.
- Lieberman, M. L. and Pierson, H. O. (1974). Carbon, 12, 233-241.
- Lieberman, M. L., Curlee, R. M., Braaten, F. H., and Noles, G. T. (1975). J. of Composite Materials 337–346.
- Loll, P., Delhaès, P., Pacault, P., and Pierre, J. (1977). Carbon 16, 390-395.
- Lucas, P. and Marchand, A. (1990). Carbon 28, 207-219.
- McAllister, P. and Wolf, E. E. (1993). AIChE Journal 39, 1196-1209.
- McEnaney, B. and Mays, T. (1993). In *Essentials of Carbon–Carbon Composites* (Ed. by C. R. Thomas, Royal Society of Chemistry), ch. 6, 143–173.
- Manocha, L. M., Bahl, O. P., Singh, Y. K. (1989). Carbon 27, 381-387.
- Marinkovic, S. and Dimitrijevic, S. (1985). Carbon 23, 691-699.
- Naslain, R., Lamon, J., Pailler, R., Bourrat, X., Guette, A., and Langleis, F. (1999). Composites; Part A. 30, 537–547.
- Ofori, J. Y. and Sortichos, S. V. (1997). Proceedings of Euro CVD-11 (Ed. by M. D. Allendorf and C. Bernard), Vol. 97–25, 536–543.
- Oh, S. M. and Lee, J. Y. (1989). Carbon 27, 423-430.
- Okuno, H., Trinquecoste, M., Derre, A., Monthioux, M., and Delhaès, P. (2002). J. of Materials 17, 1904–1913.
- Palmer, H. B. and Cullis, C. F. (1965). In *Chemistry and Physics of Carbon* (Ed. by P. L. Walker), Vol. 1, 265–325.
- Pierson, H. B. and Lieberman, M. L. (1975). Carbon 13, 159-166.
- Posman, J. A., Gunn, G., Patterson, C., Owens, J., and Simmons, C. (1998). J. Phys. Chem. B102, 3927–3929.
- Rand, B. (1993). In *Essentials of Carbon–Carbon Composites* (Ed. by R. C. Thomas, Royal Society of Chemistry), ch. 3, 67–102.
- Rovillain, D., Trinquecoste, M., Bruneton, E., Derre, A., David, P., and Delhaès, P. (2002). Carbon **39**, 1355–1365.
- Sortichos, S. V. (1991). AIChE Journal 37, 1365-1378.
- Soutric, F. (1998). PhD thesis University of Toulouse (France).
- Tesner, P. A. (1984). In *Chemistry and Physics of Carbon* (Ed. by P. L. Walker and P. A. Thrower), Vol. 19, 65–162.
- Thiele, E. W. (1939). Industrial and Engineering Chemistry 31, 916–920.
- Thomas, C. R. (1993). In *Essentials of Carbon–Carbon composites* (Ed. by C. R. Thomas, Royal Society of Chemistry), ch. 1, 1–36.
- Truinstra, F. and Koenig, J. L. (1970). J. of Composite Materials 4, 492-499.
- Van Den Breckel, C. H. J. and Bloem, J. (1977). Philips Res. Repts. 32, 134-146.
- Vaidyaraman, S., Lackey, W. S., Agrawal, P. K., Starr, T. L. (1996). Carbon 34, 1123-1133.
- Vignoles, G. L., Baconneau, O., Brauner, C. M. (2001). In ECS Proceedings, Vol. 13 (N. T. Switart, M. D. Allendorf, M. Meyjapan, and S. Seal Editions).
- Vix-Guterl, C. and Ehrburger, P. (2003). In *World of Carbon* "Fibers and composites" (Ed. by P. Delhaès, Taylor and Francis), Vol. 2, ch. 9.
- Zi Jun Hu and Hüttinger, K. J. (2002). Carbon 40, 624–628.