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THE CVI-PROCESSING OF CERAMIC MATRIX COMPOSITES

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Résumé - Les céramiques peuvent, dans des conditions particulières, être déposées à partir de précurseurs gazeux au sein de substrats poreux. Ce procédé, désigné par infiltration chimique en phase vapeur (CVI) est particulièrement indiqué pour l'élaboration des matériaux composites à matrice céramique (CMC). Le remplissage d'un pore par CVI résulte de deux phénomènes : (i) une réaction de surface et (ii) un transfert de masse des réactifs et des produits dans la phase gazeuse. En CVI isotherme/isobare, les transferts de masse se font uniquement par diffusion. Il en résulte que la CVI doit être conduite à basse température et pression réduite pour donner un dépôt homogène en épaisseur le long des pores. En CVI forcée, les transferts de masse se font par convection forcée due à un gradient de pression. De plus un gradient inverse de température est appliqué. Il en résulte une vitesse de dépôt beaucoup plus élevée. La faisabilité du procédé CVI est établie pour diverses matrices incluant le carbone et SiC.

Abstract - Under specific conditions, ceramics can be deposited from gaseous precursors within porous substrates. This technique, referred to as chemical vapor infiltration (CVI) is particularly suited to the preparation of ceramic matrix composites (CMC). Pore filling by CVI results from two simultaneous phenomena : (i) a surface reaction and (ii) mass transfers of the reactants and products in the gas phase. In isothermal/isobaric CVI, mass transfers occur only by diffusion. As a result, ICVI has to be performed at low temperatures and under reduced pressures in order to lead to a deposit homogeneous in thickness along the pores. In forced-CVI, mass transfers are by forced convection due to a pressure gradient. Moreover, an inverse thermal gradient is applied resulting both in a much higher deposition rate. The feasibility of the CVI process is established for a number of ceramic matrices including carbon and SiC.

1 - INTRODUCTION

Ceramic materials are known for their refractory character, their mechanical properties (stiffness, strength, wear resistance) both at ambient and high temperatures, their low density and, in many cases, their resistance to severe chemical environments (e.g. oxidizing atmospheres at high temperatures). They are already widely used in many fields, e.g. as coatings resistant to wear or/and oxydation. On the other hand, their use as primary structural parts, e.g. in advanced reciprocating engines or gas turbines, has been limited up to now by their brittle character. It has been established, rather recently that the toughness and reliability of structural ceramics (e.g. SiC, Si₃N₄, SiO₂-based glass-ceramics, oxides) can be dramatically improved by applying to ceramics the concept of fiber-reinforcement. As a matter of fact, ceramic matrix composites (CMC) may exhibit toughness comparable to that of light aeronautical alloys (i.e. K_{IC} values of the order of 30-50 MPa m^{1/2}) when they are correctly processed /1-4/.

The processing of structural ceramics is known to be a difficult subject in materials engineering. On the one hand, ceramic materials are characterized by a mechanical behavior which is very sensitive to defects even of very small size (i.e. of the order of a few μm and even less) and thus, should be processed very carefully. On the other hand, ceramics are very refractory materials (melting points often higher than 2500°C), a feature which precludes their processing and forming in the molten state. Furthermore, they usually do not exhibit any plasticity at low or medium temperatures (although superplastic ceramics have been recently mentioned). Thus, many ceramics (e.g. covalent SiC, Si₃N₄, B₄C) can be sintered only at high temperatures or/and with sintering aids.

The main interest of the **chemical vapor processing routes** lies in the fact that they allow the deposition of ceramics at medium and even low temperatures, depending on the nature of the activation mechanisms (typically 1000°C for thermally activated CVD and 300-500°C for plasma assisted CVD), whatever the melting point and thermal stability of the materials. Therefore, the CVD of ceramics can be performed on a variety of substrates including those with a limited thermal stability (e.g. electronic components, thermally treated steels and alloys, glasses, etc...). Moreover, since in CVD the starting materials are gaseous species, another advantage of the chemical vapor processing routes lies in the fact that they may result in very pure ceramics (gas and liquids are easily obtained with a high degree of purity). Finally, CVD-processing may lead to solids with fine grain microstructures and thus with good mechanical properties.

The advantages which have been mentioned above explain why chemical vapor deposition has been among the first processing routes selected for the preparation of CMC /5,6/. As a matter of fact, ceramic fibers, e.g. carbon or SiC-based fibers, are very strong and stiff but : (i) their diameter is very small (i.e. of the order of 10 µm and often less) and (ii) they are very sensitive to environmental effects (e.g. to surface defects resulting from handling, to temperature and to oxydation). Obviously, taking into account the nature of ceramic fibers, CMC should be prepared according to soft processing routes a requirement which precludes the use of high temperatures (e.g. sintering) and abrasive processes (e.g. pressing).

One of the objectives of the present contribution is to show that the so-called **chemical vapor infiltration (CVI)** process, which is directly derived from CVD, is well suited to the specific requirements of the elaboration of CMC. Inasmuch as the starting material is usually here a porous preform made of woven fibers, another objective of the present contribution is to show how the deposition parameters commonly used in CVD have to be modified to favor in-depth deposition (i.e. the deposition in the pore network of the substrate) over external surface coating in order to lead to a fully densified material. Finally, some information on the practical aspects of CVI, the main properties of CVI-processed CMC and examples of application will be given.

2 - BASIS OF THE CVI-PROCESS

2.1 - Definition

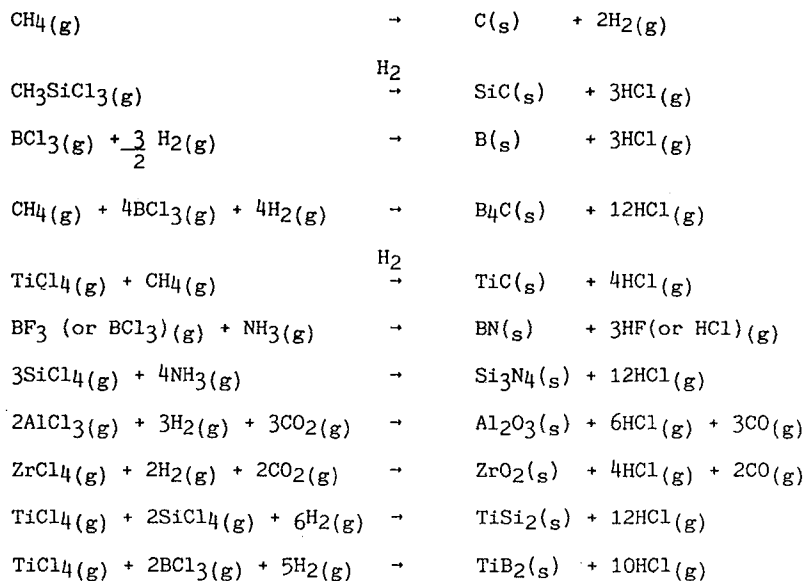
CVI is a processing technique according to which a solid (e.g. a ceramic material) is deposited, within the pore network of a heated substrate, from a chemical reaction taking place between gaseous species which flow (either by diffusion or convection) in the pores. CVI can be in principle applied to any given porous substrate as long as : (i) the pores are interconnected and large enough in diameter and (ii) the substrate is stable thermally and chemically under the CVI conditions. The aim in CVI is usually to densify as completely as possible, the substrate but the process can also be stopped at any desired state of densification /7/.

To understand the specific requirements of the CVI-processing of porous substrates, it may be useful first to recall briefly some of the features of CVD itself.

2.2 - Basis of CVD

In CVD, a solid (e.g. a ceramic) is formed as the result of a chemical reaction taking place between gaseous source species (the precursor), the other products of the reaction being gaseous under the CVD conditions. Table I gives a few examples of overall chemical reactions commonly used for the deposition of ceramics. As a matter of fact, a variety of source species are available for most covalent and iono-covalent ceramics. Halides are often selected, for economical considerations, but organometallic species are used as well. On the contrary, CVD is not well suited to the formation of ionic oxides (e.g. CaO or MgO) for lack of source species (e.g. alkaline earth chlorides are gaseous only at high temperatures).

Table I : Examples of overall chemical reactions commonly used for the formation of ceramics by CVD/CVI



The chemical reaction which leads to the deposition of the solid is usually not as simple as those given in table I : (i) intermediates and by-products are often formed and (ii) reactions are often limited. Therefore, the deposition of a given ceramic may be the result of a very complex heterogeneous chemical reaction. A computerized thermodynamic approach is frequently used to derive the main features of a given CVD system, i.e. the nature and relative amounts of the gaseous and condensed species present at equilibrium and thus the theoretical yields, as a function of the CVD-parameters (temperature, pressure and feed gas composition), assuming that equilibrium is reached in the CVD furnace (which is not necessarily the case). An example of such a treatment is given in fig. 1 for the CVD of SiC from $\text{CH}_3\text{SiCl}_3/\text{H}_2$ mixtures /5/ whereas many others are available from literature /8-14/. It clearly appears from fig. 1 that the deposit, for a given temperature and pressure, is either a single phase or a mixture of two phases (codeposits) depending on the initial composition ($\alpha = [\text{H}_2]/[\text{CH}_3\text{SiCl}_3]$ ratio). Moreover, a number of gaseous by-products are formed (e.g. silicon sub-chlorides, hydrocarbons, silanes) which lower the yield in solid /15/.

As shown in fig. 2a the mechanism according to which a solid is deposited on a substrate is complex and consists of at least three steps : (1) the source species diffuse through a boundary layer surrounding the substrate, (2) the source species after adsorption on the substrate react among themselves to give rise to the solid and to adsorbed gaseous reaction products and finally (3) the latter after being desorbed from the substrate diffuses through the boundary layer. Therefore, the deposition rate may be controlled either by mass transfer phenomena (steps (1) and (3)) or by the kinetics of surface phenomena (step (2)). Since these two different phenomena do not obey the same laws with respect to temperature, pressure and gas flow, a transition between a domain where deposition is rate-controlled by surface phenomenon kinetics to a domain where it is rate-controlled by mass transfer is often observed on the $V = f(X)$ curves (where V is the deposition rate and X one of the CVD-parameters). An example of such a transition is given in fig. 3 for the deposition of B_4C from $\text{BCl}_3\text{-CH}_4\text{-H}_2$ /16/.

The chemical reaction giving rise to the deposition of the solid should be activated. In most cases and particularly when the substrate is stable enough, the activation is obtained by heating the substrate to a high enough temperature, i.e. 800-1200°C for most inorganic source species and even much lower temperatures (e.g. 400-700°C) when

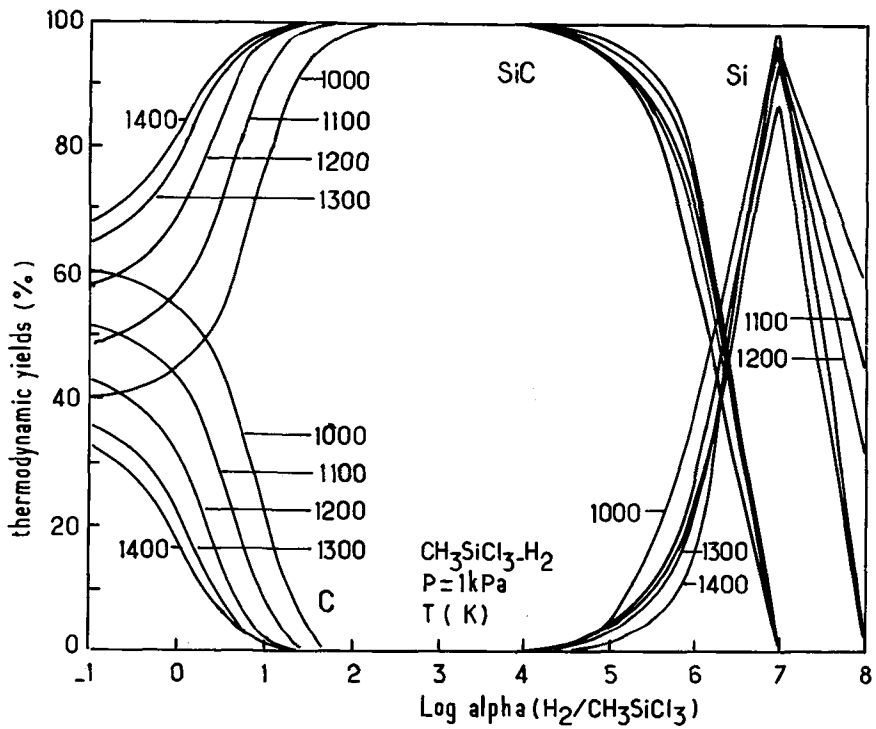


Fig. 1 : CH₃SiCl₃/H₂ CVD/CVI system. Calculated thermodynamic yields for the solid phases, as a function of $\alpha = [H_2]/[MTS]$ for various temperatures from /15/

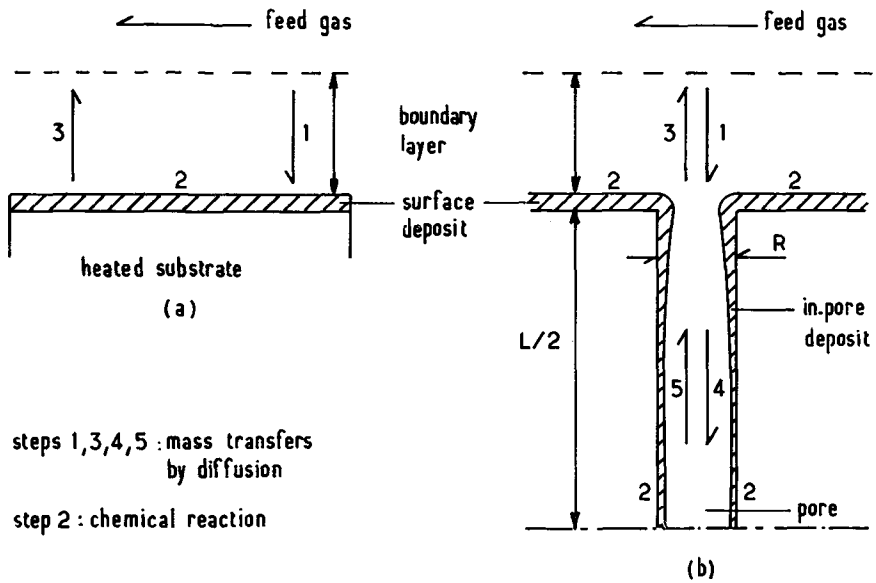


Fig. 2 : The different steps in CVD (a) and CVI (b)

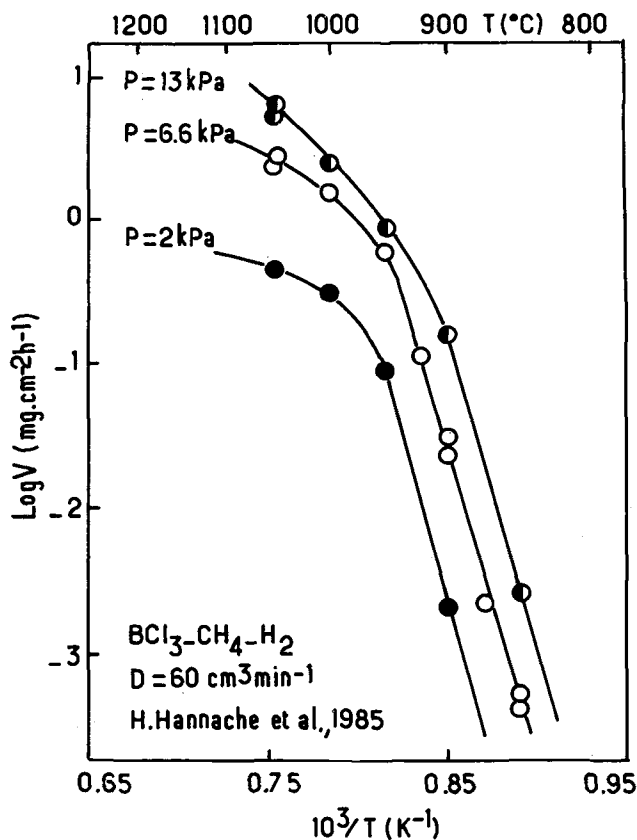


Fig. 3 : Thermal variations of the deposition rate of B₄C from BCl₃-CH₄-H₂ showing a transition from a mass transfer rate controlled regime to a regime rate controlled by surface reaction kinetics /16/

organometallic precursors are used. For specific applications, other kinds of activation may be preferred (as in plasma assisted CVD) /7/.

The microstructure of the deposit depends mainly on the nature of the substrate (which may control the initial nucleation mechanism) and the CVD-conditions (particularly the supersaturation). Facetted deposits, well-developed columnar deposits, as well as fine grain microstructures are common, the latter being the most interesting as far as mechanical properties are concerned /7/.

2.3 - Fundamentals of the CVI-process

2.3.1- Isothermal/isobaric CVI (ICVI)

The deposition of a solid on the wall of a pore with a view to fill, as completely as possible, that pore is still more complex and appears to be possible only under specific deposition conditions. In isothermal/isobaric CVI (no temperature/pressure gradients along the pore), the gaseous reactants and products are transported along the pore only by diffusion due to concentration gradients between the entrance and the bottom of the pore. Thus, as shown in fig.2b, two new steps must be added to the three steps already mentioned for CVD : (i) after having diffused through the external boundary layer (step 1) the reactants must diffuse along the pore length (step 4) in order to reach any point of the inner surface of the pore where the chemical reaction giving rise to the solid-deposit takes place (step 2) and (ii) the gaseous by-products resulting from the

deposition reaction must diffuse in the opposite direction, first along the pore length towards the pore entrance (step 5) and finally across the external boundary layer (step 3) /17/.

From the above discussion of the kinetics of CVD it seems quite obvious that CVI should be performed under conditions where the deposition process is rate-limited by surface phenomenon kinetics (step 2) and not by mass transfer of the reactants/products by diffusion in the vapor phase (steps 1, 3, 4 and 5). If this condition is not fulfilled, the deposition on the external surface of the substrate and near the pore entrance will be favored with respect to that taking place on the pore inner surface far from the pore entrance, resulting in an early sealing of the pore (which could be no longer densified). Therefore, it is imperative that ICVI be performed at low temperatures and pressures. Unfortunately, under such conditions : (i) the thermodynamic yield in solid is often low for many common CVD systems and (ii) the deposition rate is slow /8, 17/.

The filling of a pore by ICVI involves two competing phenomena : (i) the mass transfers of the gaseous species along the pore, governed by diffusion, which feed the reaction sites of the pore wall with reactants and conversely evacuate the gaseous products (steps 4 and 5) and (ii) the surface reaction which absorbs the former and releases the latter (step 2). The result of the competition can be assessed by considering dimensionless numbers which involve the kinetic constant of the surface reaction k_s , an effective diffusion coefficient D_e and a parameter representative of the pore geometry (e.g. its radius R or the L^2/R ratio where L is the pore length)/6, 19-21/. Two approaches will be discussed assuming : (i) a first order reaction, e.g. that of formation of SiC from CH_3SiCl_3 mixed with hydrogen and (ii) a pore of cylindrical geometry.

In the approach proposed by Van den Breckel et al. /18/ for the CVD of ceramics within cylindrical tubes of small diameters (i.e. $0.1 < d < 1$ mm) and then extended by J.Y. Rossignol et al. /8/ to porous fiber preforms with pores of much smaller diameters ($1 < d < 500$ μm), the dimensionless number which has been selected is the Sherwood number Sh (which is independent of both the reaction order and concentrations in the gas phase, for a first order reaction) :

$$Sh \approx \frac{k_s \cdot R}{D_e} \quad (1)$$

where k_s and D_e depend on the deposition conditions, as follows :

$$k_s = k_0 \exp \left(- \frac{E}{R^* T} \right) \quad (2)$$

with k_0 : frequency factor, E : activation energy and R^* : the perfect gas constant. Generally speaking, the expression which has to be used for D_e should include both the Fick diffusion coefficient D_F and the Knudsen diffusion coefficient D_K , which can be combined according to the following equation :

$$\frac{1}{D_e} \approx \frac{1}{D_F} + \frac{1}{D_K} \quad (3)$$

For pores of rather large diameters, Knudsen diffusion can be neglected with respect to Fick diffusion and D_e , which is equal to D_F in a first approximation, is known to depend on both T and P for a given gaseous species, according to the following equation :

$$D_F = D_0 \cdot (T)^m \cdot (P^{-1}) \quad (4)$$

where D_0 is a constant and $1.5 < m < 2$. In such a case, by combining equations (1), (2) and (4), the Sherwood number can be rewritten, as a function of P , T and R , as follows :

$$Sh = \frac{k_0 R}{D_0} \cdot P \cdot \frac{\exp(-E/R^* T)}{T^m} \quad (5)$$

The absolute value of Sh governs the morphology of the deposit in the pore. Small values of Sh , which correspond to experiments performed at low T and P for a pore of given

radius R, yield more uniform deposits along the pore length /18/.

On the other hand, for pores of small diameters (typically, $2R < 10\mu\text{m}$) Knudsen diffusion can no longer be neglected (it can even be the only mass transfer mechanism for pore of very small diameters). Under such conditions, both D_F and D_K must be taken into account and equation (3) must be used for the calculation of D_e , D_K being given according to the kinetic theory of gases by :

$$D_K = \frac{2R}{3} \left[\frac{8R^*T}{\pi M} \right]^{\frac{1}{2}} \quad (6)$$

for a gaseous species of molar mass M in a pore of radius R. It is worthy of note that D_K does not depend on the total pressure P. As a result, the expression for Sh is more complex than (5) but, generally speaking, the conclusions drawn above remain valid (at least at a high enough total pressure).

In order to illustrate the effect of T, P and R on the deposit profile in a cylindrical pore, a calculation has been done, on the basis of the Van den Brekel/Rossignol model /8, 18/ for a symmetrical straight pore open at both ends, of length $L = 10 \text{ mm}$, acting as substrate for the deposition of SiC from $\text{CH}_3\text{SiCl}_3/\text{H}_2$ precursor /22/. The calculation was done according to an incremental procedure to take into account the fact that the pore entrance radius regularly decreases vs time in a ICVI experiment finally becoming nil when the pore is sealed by the deposit, whereas in the original Van den Brekel model /18/ the deposit thickness is assumed to remain small with respect to the pore radius. For the iteration step i, the radius of the pore at a depth z (the origin being the pore entrance), i.e. $r(i, z)$, is obtained by subtracting the thickness of solid $G(i, z)$ calculated according to the Van den Brekel's model from that calculated for the step i-1, i.e. $r(i-1, z)$:

$$r(i, z) = r(i-1, z) - G(i, z) \quad (7)$$

where from /18/ :

$$G(i, z) = G(i, 0) \frac{\cosh \left[\frac{(2K)^{\frac{1}{2}} (z - L/2)}{R(i)} \right]}{\cosh \left[\frac{L}{2R(i)} (2K)^{\frac{1}{2}} \right]} \quad (8)$$

with $G(i, 0)$ as the thickness of solid deposited at $z = 0$ for step i in a pore assumed, in a first approximation, to be cylindrical and of radius $R(i)$. The iteration procedure is stopped at step p, when the pore is sealed, at its entrances, by the deposit, i.e. when $r(p, 0) = 0$ or $e(p, 0) = R$. The kinetic data for the $\text{CH}_3\text{SiCl}_3/\text{H}_2$ system were taken from Schoch et al. /23/. D_K was calculated according to equation (6) and found to be equal to $D_K = 7.95 RT^{\frac{1}{2}} m^2 s^{-1}$ for the CH_3SiCl_3 molecule whereas D_F was calculated, for the $\text{CH}_3\text{SiCl}_3/\text{H}_2$ mixtures, according to an equation of type (4), $D_F = 5.59 \cdot 10^{-5} (T)^{3/2} (P)^{-1} \text{ cm}^2 \cdot \text{s}^{-1}$ /24/. The deposit profiles are shown in fig.4 and 5 for various values of the pore diameter (100 and $1\mu\text{m}$), temperature (800 ; 900 ; 1000 and 1100°C) and total pressure (2 ; 20 and 100 kPa).

As expected, the results of the calculation show that the thickness homogeneity of the deposit is excellent when temperature and total pressure are low enough (e.g. $T = 800 - 900^\circ\text{C}$ and $P = 2 - 20 \text{ kPa}$) at least when the pore diameter is large ($2R = 100 \mu\text{m}$), i.e. for low Sherwood numbers (equation (5)). On the contrary, raising both T and P tends to favor deposition near the pore entrance. This feature is still more evident for pores of small diameters (fig. 4b and 5b). As an example, almost no deposition occurs in a pore of $1 \mu\text{m}$ in diameter beyond $L/10$ from pore entrance, for $T = 1000^\circ\text{C}$ and $P = 20 \text{ kPa}$ (fig 4b). Lowering temperature to 800°C only slightly improves the deposit profile (fig. 4b) whereas lowering total pressure to 2 kPa has no effect (inasmuch as mass transfers are thought to be already limited by Knudsen diffusion at 20 kPa) (fig. 5b).

In a somewhat different approach based on the common features that exist between ICVI and heterogeneous gas catalysis within a porous catalyst, Fitzer and his coworkers have chosen to use another dimensionless number, the second Damkohler number Da_{II} (or Thiele

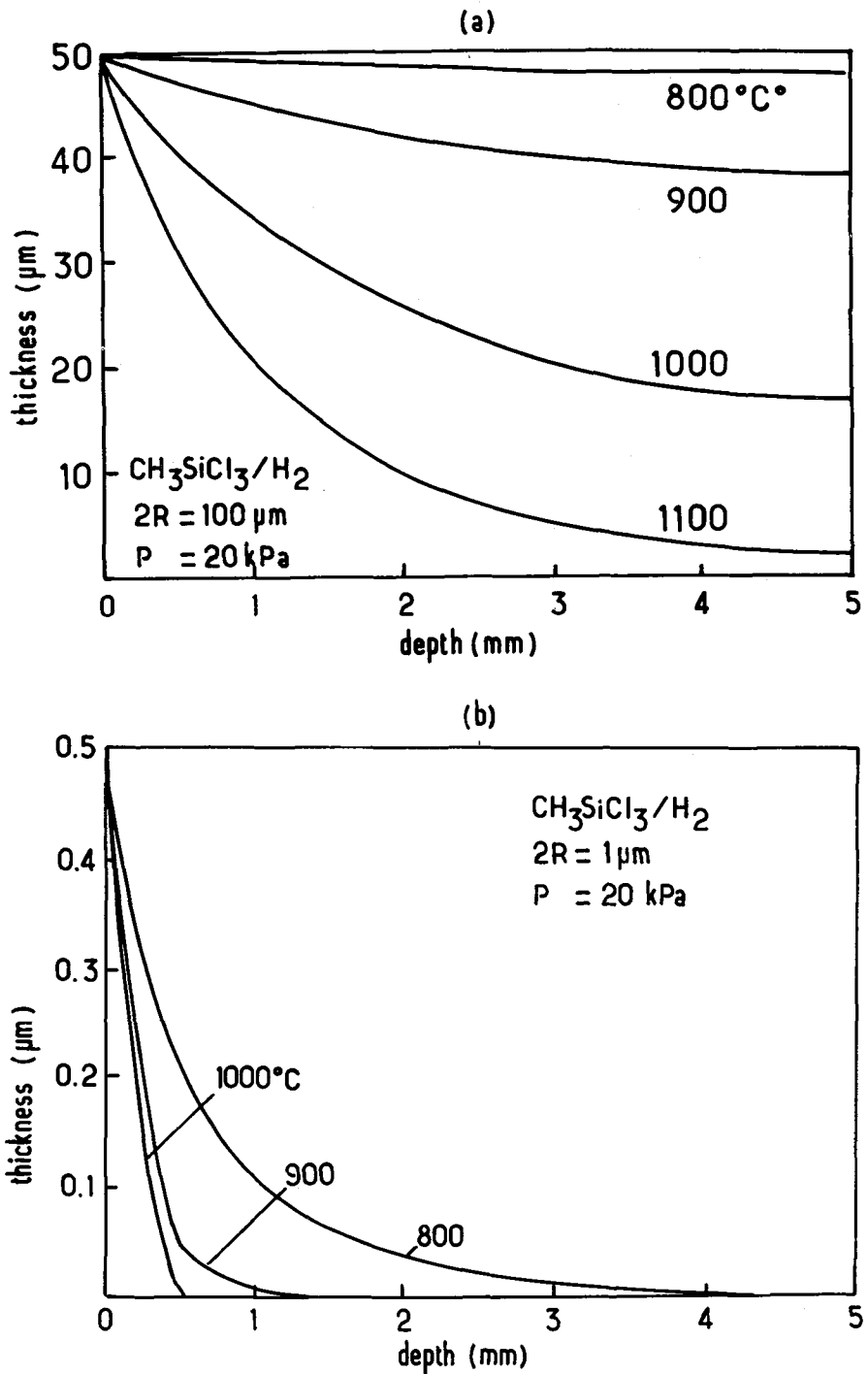


Fig. 4 : Computed in-pore deposit thickness profiles for various deposition temperatures and two pore diameters (i.e. $2R = 100 \mu\text{m}$ and $2R = 1 \mu\text{m}$)

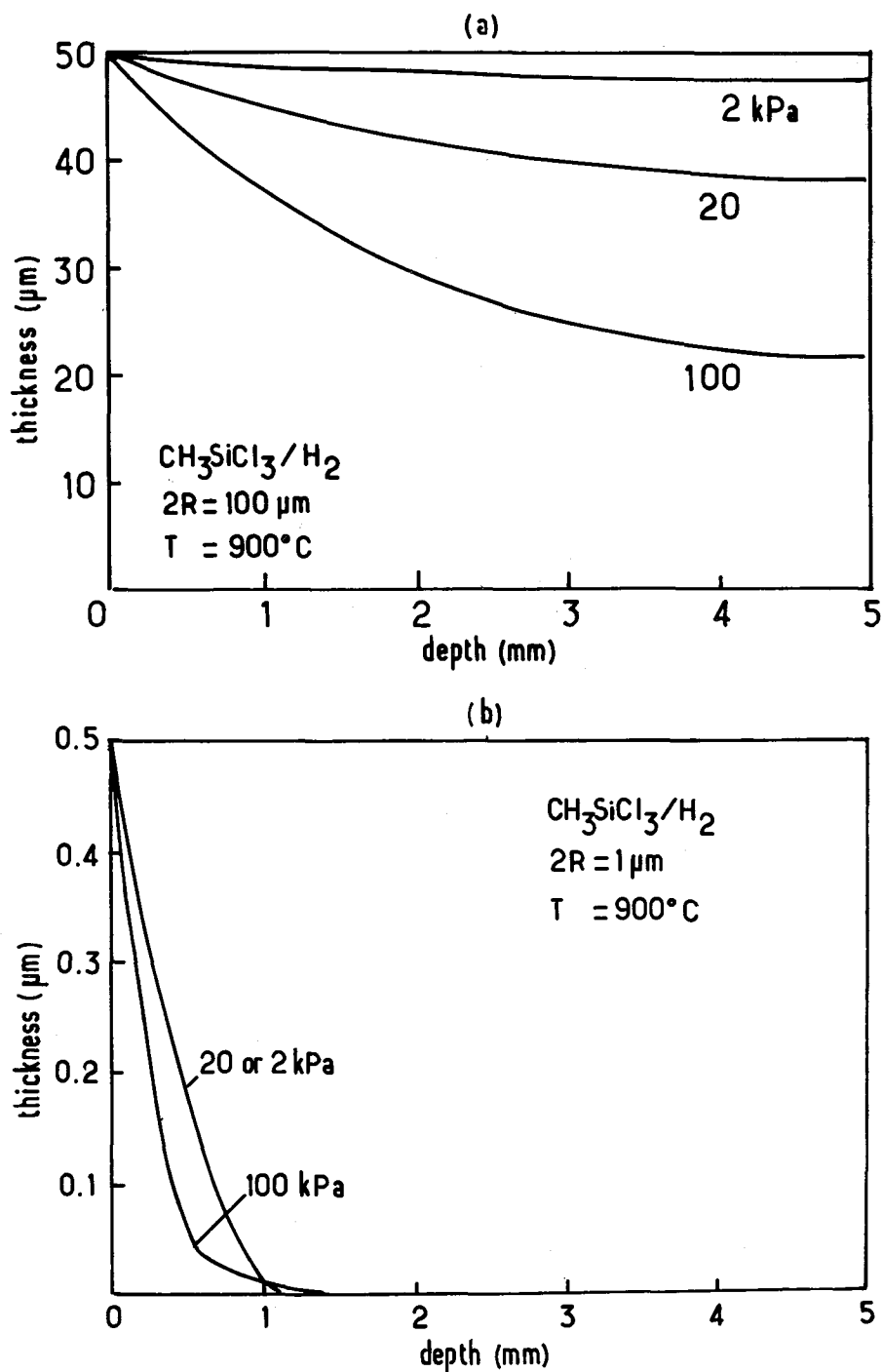


Fig. 5 : Computed in-pore deposit thickness profiles for various total pressures and two pore diameters (i.e. $2R = 100 \mu\text{m}$ and $2R = 1 \mu\text{m}$)

number ϕ) defined as follows for a first order reaction /6, 19-21, 25/ :

$$Da_{II} = \phi^2 = 2k_s L^2 / (RD_e) \tag{9}$$

and which is, as a matter of fact, closely related to the Sherwood number as emphasized by Fedou et al. /22/. Fitzer et al. defined an effectiveness factor η (which plays a role similar to the $G(i,z)/G(i,o)$ ratio in the preceding model) as the ratio between the rate of in-pore deposition and that of external surface deposition. The η factor is related to the dimensionless numbers by :

$$\eta = \frac{\tanh Da_{II}^{1/2}}{Da_{II}^{1/2}} = \frac{\tanh \phi}{\phi} \tag{10}$$

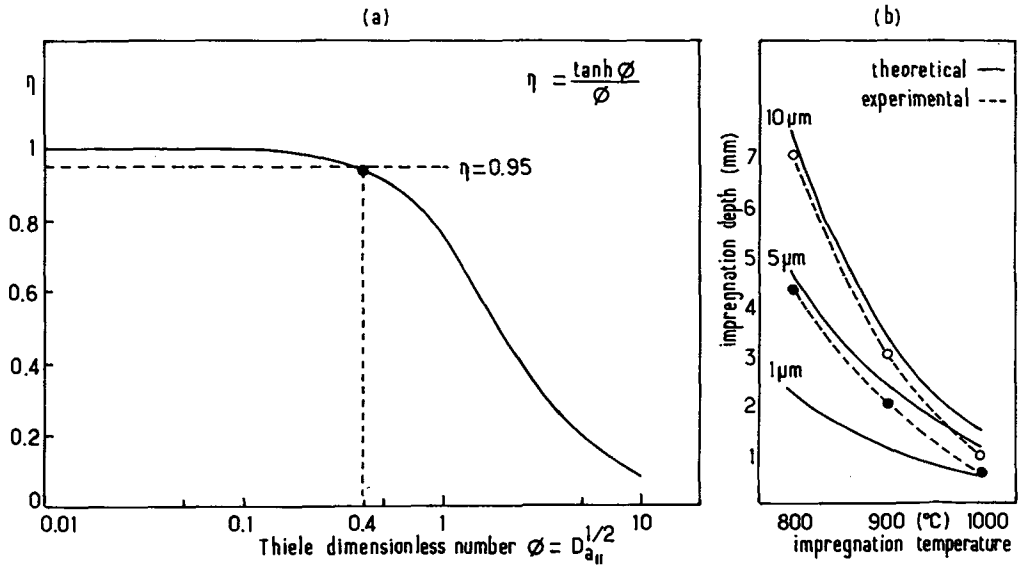


Fig. 6 : The model of Fitzer et al. : (a) variations of the effectiveness factor as a function of the Thiele number ; (b) Variations of the maximum depth of impregnation as a function of the impregnation temperature /26/

The variations of η as a function of $\phi = Da_{II}^{1/2}$ are shown in fig. 6a. In order to favor in-pore deposition, η should be as close as possible to unity. The curve shows that this condition, expressed as $0.95 < \eta < 1$, is fulfilled when $Da_{II}^{1/2} < 0.4$. When combined with equation (9), this condition defines a maximum depth for impregnation, L_{max} :

$$L_{max} \leq 0.4 \left[\frac{RD_e}{2k_s} \right]^{1/2} \tag{11}$$

The authors have calculated L_{max} for (i) model cylindrical pores (closed at one end) of large diameters ($0.4 < R < 1$ mm) and (ii) porous graphites with mean pore diameters ranging from 1 to 20 μm , filled by ICVI with SiC deposited from CH_3SiCl_3/H_2 under conditions corresponding to the regime rate-limited by surface reaction. The results of their calculations as well as their experimental data are shown in fig. 6b for pores of small diameters /26/. L_{max} appears to increase when temperature decreases and pore diameter increases, a feature which is in agreement with the Van den Breckel/Rossignol model, as discussed above.

2.3.2 - Forced flow/thermal gradient CVI (FCVI)

In CVI, the mass transfers of reactants and products along the pore are due only to diffusion with the result that deposition should be performed at low temperature and pressure in order to obtain a deposit uniform in thickness along the pore. Under such conditions, the rate of infiltration is necessarily slow.

An alternative process, referred to as FCVI, has been worked out by Caputo et al. for the infiltration of SiC and Si₃N₄ matrices in different porous media, in which the mass transfers are by forced convection resulting from a pressure gradient /27-29/. As shown schematically in fig. 7, the reactants are forced to flow along the pore under a high pressure ($P_1 = 100$ to 200 kPa) while the products (and the unreacted species) are evacuated at a lower pressure P_2 . Moreover, since the gas phase is depleted in reactants as it flows in the pore (due to the chemical reaction taking place on the pore wall), an inverse thermal gradient is applied along the pore. Since as discussed above, the surface phenomena giving rise to the deposit are thermally activated (equation (2)), the effect of the temperature increase may compensate, under optimized conditions, that of the gas phase depletion in reactants.

The competing effects of the forced gas flow and thermal gradient on the deposit profile have been justified theoretically, by Starr, for random short fiber preforms infiltrated with SiC deposited from CH₃SiCl₃/H₂ precursor, assuming a first order reaction /30/. When $T_1 = T_2 = 1200^\circ\text{C}$ (no thermal gradient), deposition is limited to the vicinity of the preform surface through which the reactants are injected, due to a very rapid depletion of the gas phase in reactants. Furthermore, the deposit profile as shown in fig. 8, is similar to that calculated for $T = 1100^\circ\text{C}$ according to the Van den Breckel/Rossignol model (fig. 4, 5). On the contrary, when T_1 is lowered to 200°C , the deposit takes place near the opposite surface of the preform (maintained at 1200°C) since the gas phase depletion is now very limited. Finally, a deposit of almost uniform thickness is obtained when T_1 is adjusted to about 1000°C .

One of the main advantage of the FCVI process lies in the fact that the infiltration time necessary to reach a given state of densification for a given porous substrate is reduced by one order of magnitude with respect to that required in ICVI due to (i) faster mass transfers (forced convection) and (ii) higher deposition temperatures (limited only by the stability of the preforms). On the other hand, the FCVI process has also important drawbacks which will be discussed in the next section.

3 - PRACTICAL ASPECTS OF THE CVI PROCESS

3.1 - Preforms

In the CVI processing of CMC, one of the important starting materials is the fibrous preform (the other being the gaseous precursor of the matrix) since its nature directly governs : (i) the volume fractions of fiber and matrix in the composite as well as (ii) the fiber orientation and degree of anisotropy. The fibers available for the reinforcement of ceramic matrices are limited to carbon and SiC -or Al₂O₃- based fibers. From a mechanical and thermal stability point of view, the best are the former but, unfortunately, the use of carbon fibers at high temperatures is limited to atmospheres which do not contain oxygen unless a protective coating, such as SiC, has been deposited on the fiber surface (e.g. by CVD) /31/. In the preform, the fibers are either short (chopped fibers or whiskers) or continuous (woven or non-woven).

A very important parameter of the preform is its porosity. On the basis of the discussion presented in section 2, the porosity of the preform should obviously be made of open interconnected pores of large enough diameters (i.e. ranging between a few μm and a few $100 \mu\text{m}$). In order to allow an easy diffusion/flow of the gaseous precursor, the pore spectrum of the preform must contain a high enough percentage of pores of large diameters.

Short fiber preforms can be made according to the slurry molding process /29/. Chopped fibers (or whiskers) are first suspended in a liquid containing a binder (e.g. a polycarbosilane for a SiC matrix). The slurry is then vacuum filtered to form a disk (or

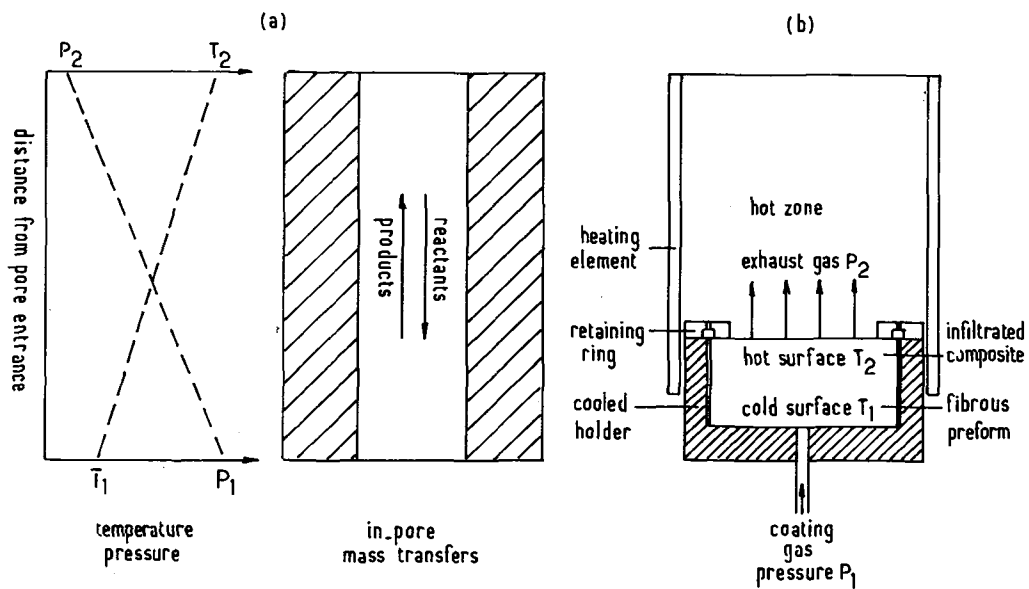


Fig. 7 : The CVI process : (a) the temperature and pressure gradients along the pore ; (b) the experimental set up (schematic) /27-29/

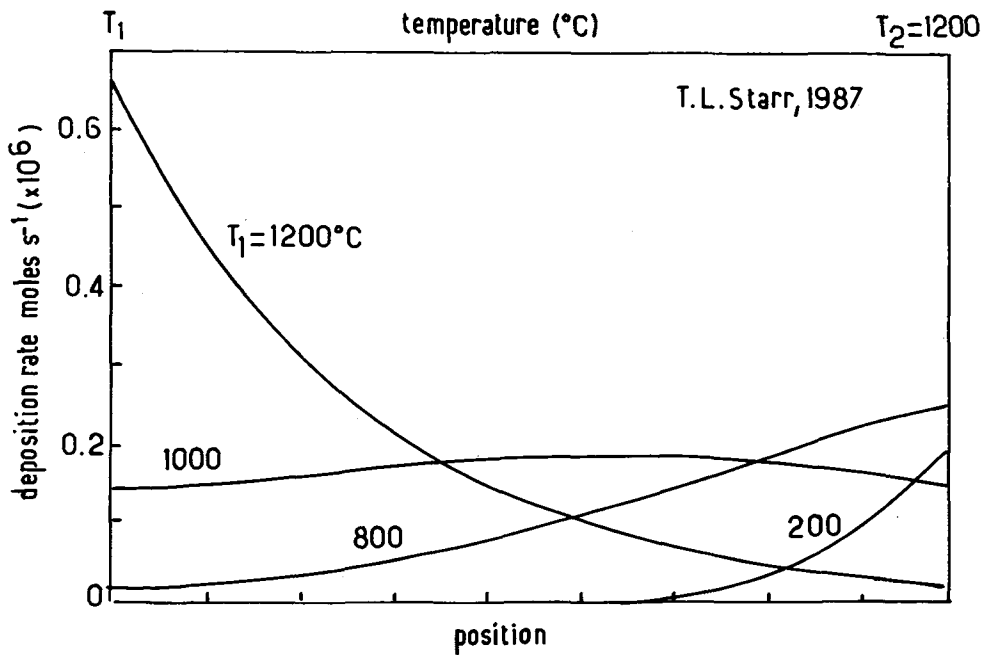


Fig. 8 : The model of Starr ; deposition profiles for various values of T_1 (T_2 being equal to $1200^{\circ}C$) /30/

any other given shape) which, after pressing (in dies or between plates) and sintering, results in a preform with a fiber volume fraction ranging between 15-25 %. Felts are also available on the market for most common ceramic fibers.

2D-preforms, made of a stack of fabrics, are the most commonly used fibrous preforms due to : (i) their high fiber volume fractions (i.e. typically 40-45 %), (ii) their pore spectra very well suited to CVI and (iii) their easy preparation. In the so-called **dry preforms**, the fabrics are pressed together with a ceramic tool (which is withdrawn after the first CVI treatment). In **consolidated preforms**, the fabrics are bonded together with an organic or organometallic binder (e.g. a polycarbosilane) that after pyrolysis will yield a small amount of a ceramic matrix, prior to the CVI-treatment. More complex **nD preforms** (with $n > 2$, n being the number of fiber orientations) can be prepared according to a similar procedure /3, 29, 32/.

Finally, **1D-preforms** are made from aligned fiber tows (maintained together, as said above, either with a ceramic tool or with a binder). Their main advantage lies in the fact that still higher fiber volume fractions can be achieved (e.g. 50-60 %). On the other hand, in such preforms, the pores are essentially unidirectional and difficult to densify. **Cross ply preforms** are made according to the same processing technique.

3.2 - Densification of the preform by ICVI

In ICVI, the preforms are set in a hot wall isothermal deposition chamber fed with a flow of the gaseous precursor (see table I) under a reduced pressure whose value depends on the pore spectrum of the preform and nature of the precursor /32/. As discussed in section 2, too high a temperature and a pressure rapidly result in an early pore sealing. Therefore, the deposition parameters should be controlled very carefully during the whole infiltration process. Table II gives the CVI-parameters for some ceramic matrices for lab-scale apparatus (most porous substrates are 2D preforms). The unreacted source species and the gaseous reaction products are pumped through traps (most of these species being corrosive when halide precursors are used).

Table II : Deposition parameters for the ICVI or FCVI of ceramic matrices in porous substrates.

Matrix	Precursor	Temperature (°C)	Pressure (kPa)	Precursor Composition	CVI-type and reference
SiC	MTS/H ₂ MTS/H ₂	900 - 1100 1050	10 - 100 3	H ₂ : MTS = 5 - 10 -	ICVI /5/ ICVI/26/
B ₄ C	BCl ₃ /CH ₄ /H ₂	900 - 950	1 - 5	BCl ₃ : H ₂ = 1 BCl ₃ : CH ₄ = 4	ICVI /16/
TiC	TiCl ₄ /CH ₄ /H ₂	950	1 - 5	H ₂ : CH ₄ = 10	ICVI /8/
Si ₃ N ₄	SiCl ₄ /NH ₃	900 - 1000	-	-	ICVI /19/
BN	BF ₃ /NH ₃	1000 - 1100	1 - 5	MH ₃ : BF ₃ = 1 - 3	ICVI /9/
Al ₂ O ₃	AlCl ₃ /H ₂ /CO ₂	950 - 1000	2 - 3	H ₂ : CO ₂ ≈ 1	ICVI /33/
ZrO ₂	ZrCl ₄ /H ₂ /CO ₂	900 - 940	1 - 5	H ₂ : CO ₂ ≈ 1	ICVI /34/
SiC	MTS/H ₂	1100 - 1200	100 - 200	H ₂ : MTS = 10	FCVI /27, 28/
Si ₃ N ₄	SiCl ₄ /NH ₃ /H ₂	-	-	-	FCVI /28/

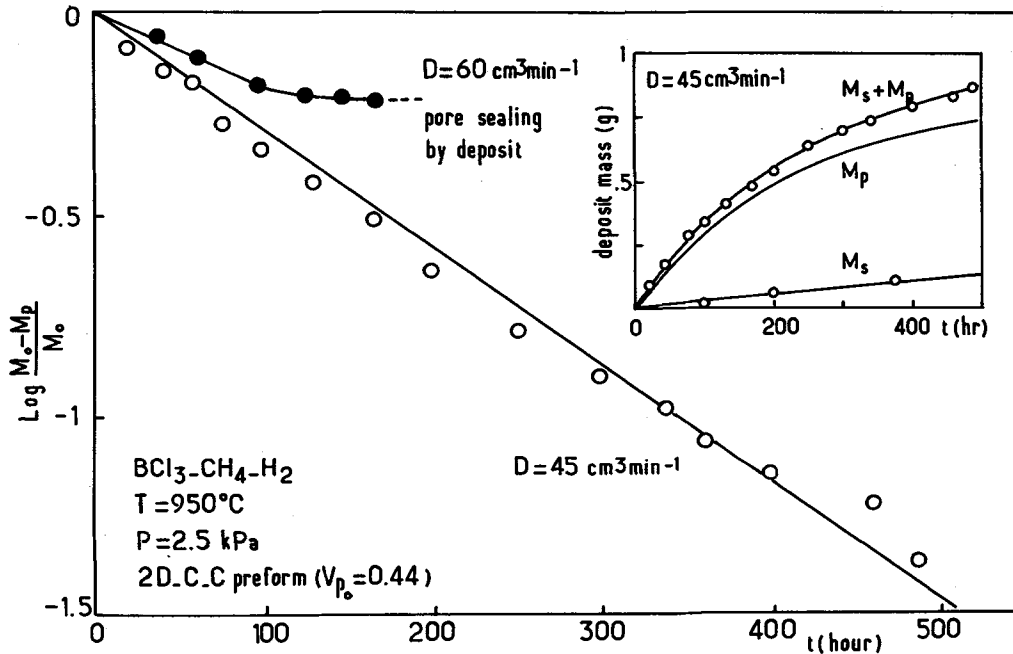


Fig. 9 : Kinetics of densification of a porous 2D-C-C preform by B_4C shown on a semi-logarithmic scale (M_0 : maximum mass of B_4C corresponding to a total filling of the porosity ; M_p : mass of B_4C deposited in the pores ; M_s : mass of B_4C deposited on the external surface). Insert : kinetics of densification shown on an arithmetic scale /16/

As discussed in section 2 and shown in fig. 9 (insert), the rate of infiltration in ICVI is slow /16, 17/. Furthermore, it decreases regularly as the infiltration proceeds (the pores becoming narrower, mass transfers by diffusion, for given T, P, are more and more difficult). When the infiltration parameters are properly optimized, the initial open porosity can be almost totally filled with the ceramic deposit (down to a residual porosity of 5-10 %) without surface machining. However, in order to reduce the infiltration duration, it may be preferable for economical considerations to re-open the pores or enlarge the pore entrances by surface machining of the preforms. A sealing of the pores is easily identified from a semi log-plot of the variations of the residual porosity vs time (deviation from a straight line).

Even under optimized infiltration conditions, the thickness of the ceramic matrix deposited in the pores is usually higher near the external surface of the preforms than in the core (due to the depletion of the gas phase in source species, as discussed in section 2). Therefore, there is usually (i) a density gradient in CMC obtained by CVI (the density being higher near the external surface) and (ii) some residual porosity.

The nature of the matrix obtained by CVI can be easily modified by changing that of the precursor injected in the infiltration chamber. As an example, the interphase material, i.e. pyrocarbon or hex-BN (used to control the fiber-matrix bonding and protect the fibers against the notch effect arising from the microcracking of the matrix, when the composite is loaded at a high enough stress) is deposited first as a thin layer (from hydrocarbon or BF_3 (or BCl_3)/ NH_3 precursors). Then the ceramic matrix itself is deposited by changing the precursor (e.g. $\text{CH}_3\text{SiCl}_3/\text{H}_2$ for SiC). Finally a coating (deposited under CVD conditions) may be applied to improve the resistance of the composite with respect to

the environmental effects.

Finally, an important advantage of the ICVI processing of CMC lies in the fact that a large number of preforms even of complex shapes can be treated simultaneously in the same infiltration chamber (the number being limited only by space considerations). This advantage compensates the low infiltration rates due to mass transfers by diffusion.

3.3 - Densification of the preform by FCVI

As shown schematically in fig. 7b, in FCVI each preform has to be set in a specific holder in order to generate the thermal gradient and to force the feed gas to flow in the pore network under pressure. At the beginning of a run, the reactants flow both axially and radially in the preform. However, the upper surface of the preform becomes rapidly coated due to the high T_2 temperature value (typically 1100-1200°C for SiC deposited from $\text{CH}_3\text{SiCl}_3/\text{H}_2$). Therefore, under such conditions the feed gas must flow radially to the void around the preform and escape through holes in the retaining ring. Moreover, since in the particular case of SiC the deposited matrix is a good heat conductor, the hot region of the preform at T_2 moves from the top toward the bottom and circumference /27-29/.

The pressure which has to be applied to force the feed gas to flow across the preform depends on the pore geometry and spectrum. P_1 values of the order of 100-200 kPa are reported for the infiltration of say 2D-SiC (Nicalon) preforms by SiC deposited from $\text{CH}_3\text{SiCl}_3/\text{H}_2$ /27-29/.

The main advantage of FCVI is to shorten, by one order of magnitude, the densification duration for a given preform with respect to ICVI, due to (i) higher deposition temperatures and (ii) faster mass transfers of the reactants and products by forced convection. However, the increase in deposition temperature may be limited by the thermal stability of the fibers. This is typically the case for the ex-polycarbosilane fibers (e.g. Nicalon fibers) whose microstructure begins to coarsen at 1100°C (with a lowering of the failure strength). Under such conditions, the only advantage of the FCVI process is related to faster mass transfers of the gaseous species resulting from forced convection.

4 - MAIN PROPERTIES AND APPLICATIONS OF CVI-PROCESSED CMC

The main interest of fiber reinforced ceramics lies in their non-brittle mechanical behavior and improved reliability with respect to their unreinforced counterparts, as shown in fig. 10 /3, 4, 28, 35/. However, this non-brittle character is observed only for well-processed materials, i.e. when : (i) the fibers are not damaged during the composite processing, (ii) the fibers are only weakly bonded to the matrix through a soft interphase (e.g. a thin layer of pyrocarbon or hex-BN) and (iii) both the fibers and their interphases are protected against environmental effects e.g. by protective coatings. Under such conditions, fibrous ceramic matrix composites : (i) obey a non linear stress-strain law (fig. 10a) and (ii) exhibit both a high resistance to crack propagation and a high failure energy (fig. 10b and 10c) due to different damaging mechanisms (e.g. matrix microcracking, fiber-matrix debonding and friction, fiber pull out) which absorb energy. It is worthy of note that the processing requirements mentioned above are perfectly fulfilled by the CVI technique.

Although the feasibility of the CVI-process has been established for different matrices, the only materials which are produced on an industrial basis are carbon-carbon, on the one hand, and C-SiC or SiC-SiC on the other hand. As far as we know, most of them are processed according to the ICVI process, the low infiltration rates being compensated by the fact that large numbers of parts can be simultaneously treated, as discussed in section 2 and 3. Carbon-carbon parts are used in rocket engines, heat shields, brake disks and prosthetic devices. SiC-based composites are used in gas turbines, reusable thermal protections and more generally speaking for structural parts used at high temperatures and under atmospheres containing oxygen.

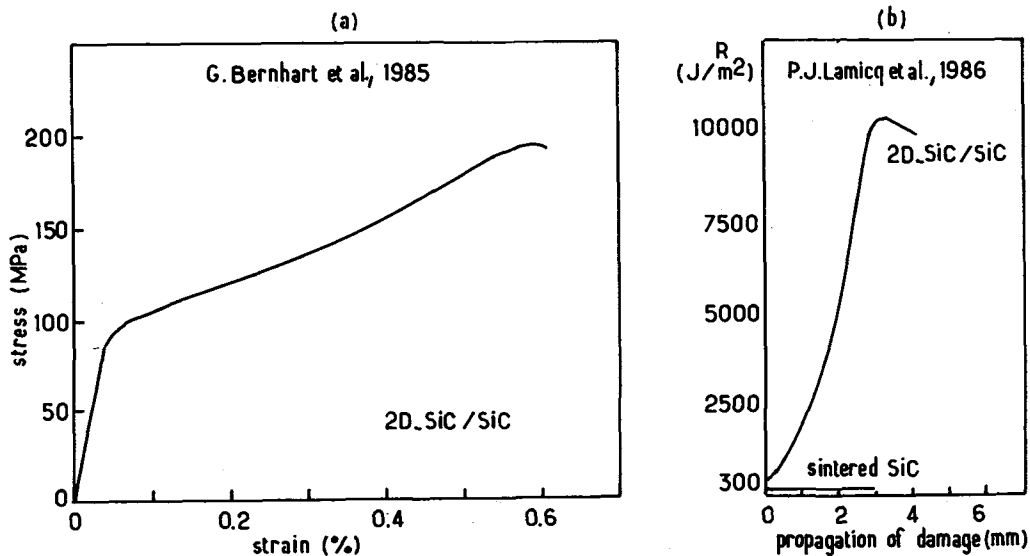


Fig. 10 : The non-brittle behavior of SiC-SiC fibrous composites at room temperature : (a) stress-strain curve in tension /3/, (b) resistance to crack propagation /4/

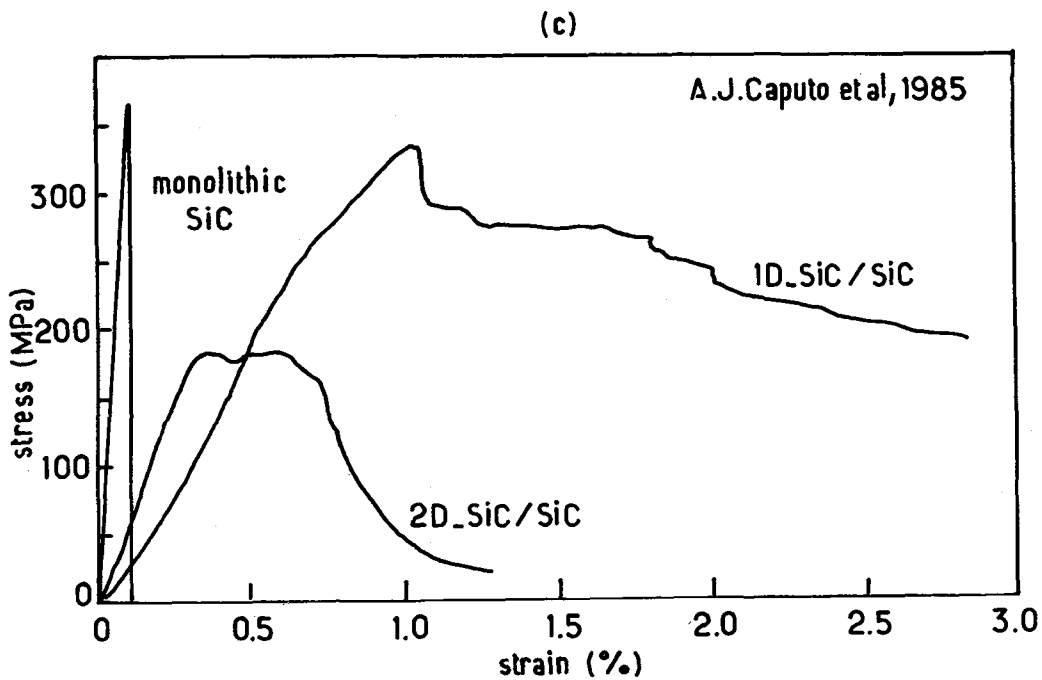


Fig. 10 : (c) stress-strain curve in 3 point-bending /27, 28/

REFERENCES

- /1/ Prewo, K.M., Brennan, J.J. and Layden, G.K., *Ceram. Bull.*, 65/2 (1986) 305
- /2/ Naslain, R., Rossignol, J.Y., Quenisset, J.M., and Langlais, F., in "Introduction aux Matériaux Composites" vol. 2 - Matrices Métalliques et Céramiques (Naslain, R., ed.), chap. 18, pp. 439-491, Coédition CNRS/IMC, Bordeaux, 1985
- /3/ Bernhart, G., Lamicq, P. and Mace, J., *L'industrie Céramique* 790/1 (1985) 51
- /4/ Lamicq, P.J., Bernhart, G.A., Dauchier, M.M. and Mace, J.G., *Ceram. Bull.*, 65/2 (1986) 336
- /5/ Christin, F., Naslain, R., and Bernard, C., *Proc. 7th Int. Conf. CVD* (Sedwick, T.O. and Lydtin, H., eds), *The Electrochem. Soc.*, Princeton, 1979, pp. 499-514
- /6/ Fitzer, E., Hagen, D., and Strohmeier, H., *Rev.Int. Hautes Temper. Refract.*, 17 (1980) 23
- /7/ Stinton, D.P., Besmann, T.M., and Lowden, R.A., *Ceram. Bull.*, 67/2 (1988) 350
- /8/ Rossignol, J.Y., Langlais, F., and Naslain, R., *Proc. 9th Int. Conf. CVD* (Robinson, Mc. D. et al., eds.), *The Electrochem. Soc.*, Pennington, 1984, pp. 596-614
- /9/ Hannache, H., Naslain, R., and Bernard, C., *J. Less-common Met.*, 95 (1983) 221
- /10/ Lhermitte-Sebire, I., Colmet, R., Naslain, R., and Bernard, C., *J. Less-common Met.*, 118 (1986) 83
- /11/ Minet, J., Langlais, F., Naslain, R., and Bernard, C., *J. Less-common Met.*, 119 (1986) 219
- /12/ Fischman, G.S. and Tetuskey, W.T., *J. Amer. Ceram. Soc.*, 68/4 (1985) 185
- /13/ Bernard, C., Deniel, Y., Jacquot, A., Vay, P.; and Ducarroir, M., *J. Less-common Met.*, 40 (1975) 165
- /14/ Ducarroir, M., Jaymes, M., Bernard, C., and Deniel, Y., *J. Less-common Met.*, 40 (1975) 173
- /15/ Prebende, C., Langlais, F., Naslain, R., and Bernard, C., *J. Less-common Met.*, (to be published)
- /16/ Hannache, H., Langlais, F., and Naslain, R., *Proc. 5th European Conf. CVD* (Carlsson J.O. and Lindström, J., eds.), pp. 219-233, Uppsala, Sweden, 1985
- /17/ Naslain, R., and Langlais, F., *Mater. Sci., Res.*, 20 (1986) 145
- /18/ Van Den Brekel, C.H.J., Fonville, R.M.M., Van Der Straten, P.J.M. and Verspui, G., *Proc. 8th Int. Conf. CVD-Paris* (Blocher, J.M. et al. eds.), *The Electrochem. Soc.*, Pennington, 1981, pp. 142-156
- /19/ Fitzer, E., *Proc. Int. Symp. Factors in Densification and Sintering of Oxide and Non-oxide Ceramics*, Hakone, Japan, 1978, pp 40-76
- /20/ Fitzer, E. and Hegen, D., *Angew Chem. Int. Ed. Engl.*, 18 (1979) 295
- /21/ Fitzer, E., Fritz, N., and Gadow, R., *Proc. Adv. Ceram. Mater.*, Yokohama, Oct. 1983 (Somiya, S., ed.), KTK Scientific, Tokyo, 1985
- /22/ Fedou, R., Langlais, F. and Naslain, R., *J. Less-common Met.* (to be published)
- /23/ Schoch, G., Fritz, W., and Fitzer, E., *Techn. Rept.*, EURAM Contract MAIE/0018/C, 1988
- /24/ Bird, R.B., Stewart, W.E., and Lightfoot. E.N., *Transport Phenomena* (Wiley, ed.), New York, 1960
- /25/ Thiele, E.W., *Ind. and Engineering Chem.*, 31/7 (1939) 916
- /26/ Fitzer, E., and Gadow, R., *Ceram. Bull.*, 65/2 (1986) 326
- /27/ Stinton, D.P., Caputo, A.J. and Lowden, R.A., *Ceram. Bull.*, 65/2 (1986) 347
- /28/ Caputo, A.J., Lackey, W.J. and Stinton, D.P., *Proc. 9th Ann. Conf. Composites and Adv. Ceram. Mater.*, Cocoa Beach, Fl. (Gac, F.D., ed.), *The Amer. Ceram. Soc.*, Columbus, Ohio, 1985, pp. 694-706
- /29/ Caputo, A.J., Lowden, R.A. and Stinton, D.P., ORNL/TM-9651, June 1985, available from NTIS, US Dept. Commerce, Springfield, VA, réf. A03
- /30/ Starr, T.L., *Proc. 10th Int. Conf. CVD-Honolulu* (G.W. Cullen, ed.), *The Electrochem. Soc.*, 1987, pp. 1147-1155
- /31/ Vincent, H., Bonnetot, B., Bouix, J., Mourichoux, H., and Vincent, C., this volume
- /32/ Naslain, R., Rossignol, J.Y., Hagenmuller, P., Christin, F., Heraud, L., and Choury, J.J., *Rev. Chimie Minérale*, 18 (1981) 544
- /33/ Colmet, R., Lhermitte-Sebire, I., and Naslain, R., *Adv. Ceram. Mater.*, 138/2 (1986) 221
- /34/ Minet, J., Langlais, F., and Naslain, R., *Composites Sci. Technology* (to be published)
- /35/ Bouquet, M., Birbis, J.M., Quenisset, J.M., and Naslain, R., *Proc. 6th Int. Conf. Composite Mater. London* (Matthews et al., eds.) Elsevier Applied Sci., London, 2 (1987) 48