



HAL
open science

Processing of (PyC/TiC) n multilayered coatings by pulsed CVD and RCVD

O. Rapaud, H. Vincent, C. Vincent, Sylvain Jacques, J. Bouix

► **To cite this version:**

O. Rapaud, H. Vincent, C. Vincent, Sylvain Jacques, J. Bouix. Processing of (PyC/TiC) n multilayered coatings by pulsed CVD and RCVD. Journal de Physique IV Proceedings, 2001, 11 (PR3), pp.Pr3-391-Pr3-398. 10.1051/jp4:2001350 . hal-02976987

HAL Id: hal-02976987

<https://hal.science/hal-02976987>

Submitted on 23 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Processing of (PyC/TiC)_n multilayered coatings by pulsed CVD and RCVD

O. Rapaud, H. Vincent, C. Vincent, S. Jacques, J. Bouix

Laboratoire des Multimatériaux et Interfaces,
UMR-CNRS 5615,
Université Claude Bernard - Lyon I
Bât 731, 43 boulevard du 11 Novembre 1918,
F-69622 Villeurbanne Cedex

Abstract. Pyrocarbon/titanium carbide (PyC/TiC)_n multilayered coatings have been deposited on carbon substrates by P-RCVD which is a combination of pulsed chemical vapour deposition (P-CVD) with reactive CVD (RCVD). From thermodynamic calculations, a thin TiC sublayer deposited between two PyC sublayers should be stoichiometric. TiC and PyC growth rates have been investigated, as well as PyC consumption occurring during carbide growth by P-RCVD. Hence, this process allows to achieve a sharp control of each sublayer thickness. Furthermore, it seems possible to totally consume the PyC intercalated between adjacent carbide sublayers in order to obtain a multilayered carbide (TiC)_n. This method has been achieved to carbon fibre coating. The very first mechanical tests carried out on coated fibres are encouraging. The next step of this work lies in the study of such sub-micrometric coatings as interphases in ceramic matrix composites.

1. INTRODUCTION

The mechanical behaviour of ceramic matrix composites (CMCs) depends on the component intrinsic properties and the strength of the fibre-matrix (F/M) interface. When this F/M bonding is too strong, a crack initiated in the brittle matrix propagates in mode I (load applied along the fibre direction), without any significant deflection, first within the matrix, then across the F/M interface and finally in the fibres themselves. This kind of composite exhibits a brittle behaviour. When the F/M bonding is weak enough, the crack propagation can be deflected from mode I to mode II parallel to the fibre axis at the interface, and a damageable non-brittle behaviour is observed. In this case, the F/M interface zone acts as a "mechanical fuse" [1, 2].

The fibre/matrix coupling can be tailored by depositing on the fibre (before depositing the matrix) a sub-micrometer thin film called "interphase", consisting of a material with a low stiffness and a low shear strength. A layered structure such as pyrolytic carbon (PyC) could fulfil these requirements.

However, PyC is not stable in an oxidising environment. Replacing, in the interphase, part of the pyrocarbon by carbide sublayers has been suggested as a way to protect the pyrolytic carbon against oxidation. This procedure leads to the concept of multilayered (PyC/carbide)_n interphase, where n is the number of PyC-carbide bilayers (figure 1a).

Bertrand *et al.* have demonstrated that, compared with a classical PyC interphase, nanoscale (PyC/carbide)_n interphases deposited by low pressure pulsed chemical vapour deposition (P-CVD) can improve the oxidation resistance of CMCs [3]. However, owing to the presence of PyC intercalated between adjacent carbide protective sublayers, the material remains sensitive to oxidation.

In previous work in this laboratory [4, 5], thin carbide (M_xC) layers were obtained on carbon fibres by reactive CVD (RCVD) method in which only the M element of the carbide is carried by the gas phase, carbon being supplied by the substrate itself. Hence, during the growth of a carbide layer by RCVD, it is possible to consume a previously deposited PyC sublayer.

The aim of the present work was to combine both methods (P-CVD and RCVD) in order to obtain multilayered carbide coatings without PyC intercalated between carbide sublayers. Such a lamellar carbide processed by pulsed RCVD (P-RCVD) should play the role of an interphase in CMCs (figure 1b).

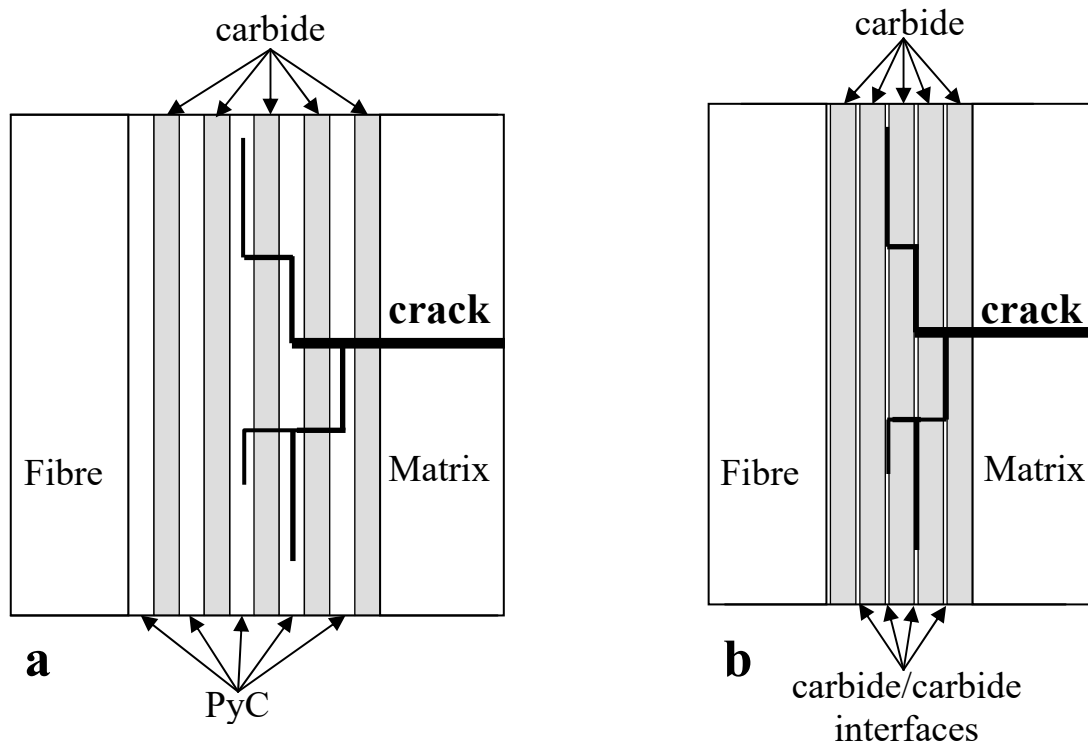


Figure 1. Schematics of multilayered interphases showing crack deflections. (a) (PyC/carbide)₅ interphase processed by P-CVD; (b) (carbide)₅ interphase processed by P-RCVD.

2. EXPERIMENTAL PROCEDURE

2.1 P-RCVD apparatus

The schematic diagram of the apparatus used for P-RCVD processing is shown in figure 2. The deposition chamber was a vertical silica tube of 300 mm in length and 28 mm in diameter. A graphite crucible was heated by induction. The gaseous precursor phase was fed to the reactor through a pneumatic valve. The temperature was monitored with an optical pyrometer. An outlet pneumatic valve permitted evacuation of the gas mixture from the reactor chamber to the vacuum pump through liquid nitrogen traps. An automatic device controlled the opening and closing of the valves and the number of pulses. A pressure sensor was placed after the reactor.

According to Dupel *et al.* [6], the pulse consists of three successive stages (figure 3):

- introduction phase, corresponding to the gas mixture introduction in the reactor, during the introduction time t_i (typically equal to 0.1 s),
- deposition phase, when the deposition reaction actually occurs, expressed by t_r ($t_r = 5$ s was used in our case),
- gas evacuation phase, characterised by t_e (typically equal to 4 s).

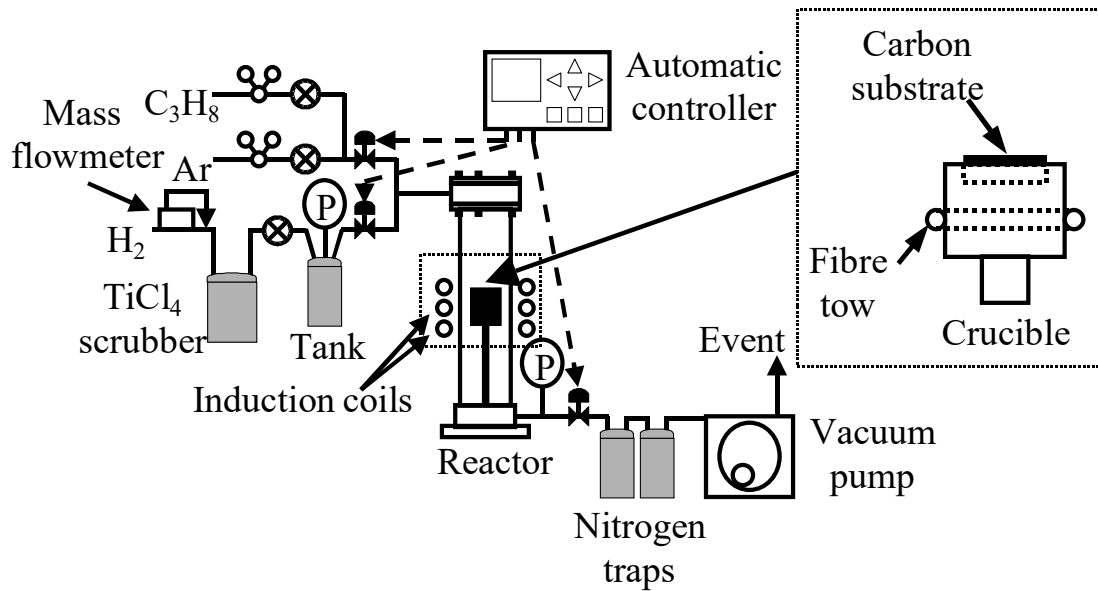


Figure 2. P-RCVD experimental apparatus. (Insert: crucible placed inside the reactor)

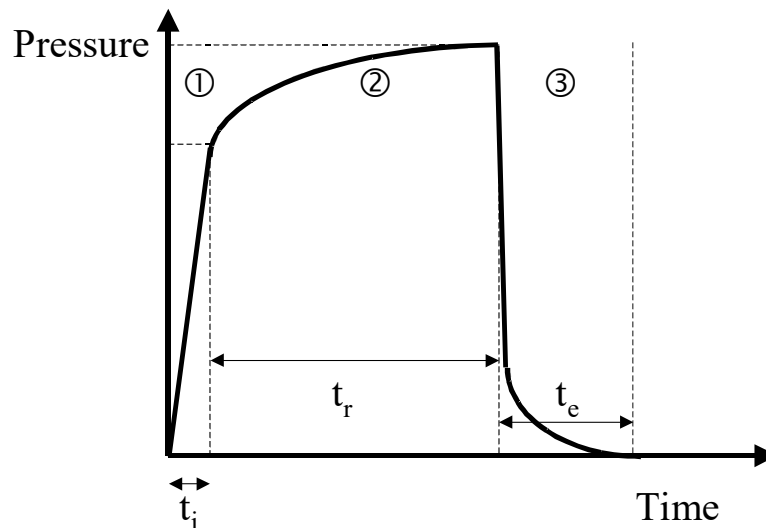


Figure 3. Example of pressure cycling: (1) introduction, deposition, gas evacuation.

For PyC deposition, propane was the gas precursor; argon was used to dilute propane. The reactant concentration ratio was: $[\text{Ar}]/[\text{C}_3\text{H}_8] = 4$. The supply pressure was 10 kPa. PyC was deposited at different temperatures.

For carbide (M_xC) deposition, titanium was chosen as the M element because of its high reactivity towards carbon. Moreover, carbon can easily diffuse through the obtained carbide: TiC (more especially as the TiC is sub-stoichiometric [7]). Once the TiC growth has started from the reaction between PyC substrate and the gas, the processing is continuing: carbon diffuses from the substrate through the TiC layer to the surface and still reacts with the gas. The precursor gas of titanium was TiCl_4 . The titanium tetrachloride vapour was carried by hydrogen through a gas bubbler and a tank at room temperature. H_2 is used as both a carrier gas and a reactant gas. The reactant concentration ratio was: $[\text{H}_2]/[\text{TiCl}_4] = 59.6$. The supply pressure was 50 kPa and the temperature was 1150°C for TiC deposition by P-RCVD.

2.2 Substrates

Bulk planar polycrystalline graphite substrates were used in this work (Ellor 10, from Carbone Lorraine). The open porosity [8] ranged from $1.0\ \mu\text{m}$ to $1.7\ \mu\text{m}$ in diameter, determined by mercury porosimeter. The specific surface was assessed to be $0.8\ \text{m}^2\text{g}^{-1}$. Bulk substrates were mechanically machined to

cylindrical samples having a 10 mm diameter and a 2 mm thickness. Before deposition experiments, samples were gradually surface polished on one side and cleaned in an ultrasonic cleaner with ethanol as solvent. Then they were placed in a drier at 100°C for one hour. The sample was positioned perpendicularly to the gas flow inside a graphite crucible heated by induction. FT500 carbon fibres (from Tonen) were used for thin multilayered coating deposition. In this case, one single tow including 3000 fibres of 10 µm in diameter was wound round the crucible (insert figure 2). The deposition conditions were the same as those for planar substrates.

2.3 Characterisation

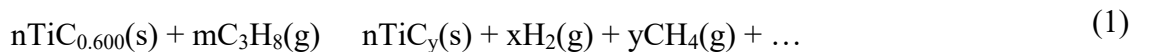
The thickness of the deposits was measured by scanning electron microscopy (SEM) after transversal cutting, resin embedding and conventional polishing. In this work, the thickness of the deposits was investigated as a function of the number of pulses (n_p). Textural characteristics were obtained by SEM (Hitachi S800). Tensile tests were performed at room temperature on coated fibres (separated at random from the treated tow) and on uncoated fibres (as a reference) with a MTS-Adamel DY-22 tensile machine (Ivry sur Seine, France) equipped with a 5 N load cell. The crosshead speed was 0.1 mm/min. In each case, a batch of about 50 monofilaments was tested with a 20 mm gauge length. The strain was corrected for system compliance. Fibre diameters were measured by laser diffractometry. The protocol and the statistic calculations were carried out using Weibull distribution with respect to Langlois [9] and Patankar [10]. The characteristic fibre failure stress $\sigma_{r(0.632)}$ was determined with an associated probability of failure $P_r = 63.2\%$.

2.4 Thermodynamic previsions

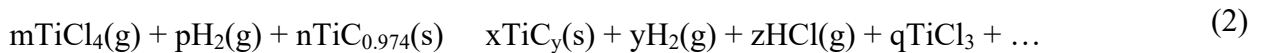
TiC has a broad domain of non-stoichiometry and the compositional limits of TiC_y are: $0.54 < y < 0.98$ [11]. Moreover, a TiC layer deposited by RCVD is expected to exhibit a compositional gradient from stoichiometric near the carbon substrate to non-stoichiometric near the external surface.

Thermodynamic calculations of two reactions which may occur during the process were made by minimisation of the Gibbs free enthalpy (thermodynamic computation with Gemini 2, from Thermodata, France, which allows calculations on non stoichiometric TiC_y in the range $0.600 \leq y \leq 0.974$) under isotherm/isochore conditions and with the parameters used for the P-RCVD process. The temperature was 1150°C, and total pressure fixed to 10 kPa.

The first considered reaction was the action of gaseous propane on solid non-stoichiometric titanium carbide.



The second one was the action of the TiC gaseous precursor mixture on quasi-stoichiometric titanium carbide.



These calculations allowed to obtain the composition of TiC_y and the quantity of each species at the equilibrium. From these calculations, qualitative tendencies could be extracted.

3. RESULTS AND DISCUSSION

3.1 P-CVD of PyC

From figure 4a, we could obtain the average PyC deposition rate R_{PyC} , for three temperatures: at $T = 1150^\circ C$, $e^{PyC}_{1150} = 48$ nm/pulse, at $T = 1100^\circ C$, $e^{PyC}_{1100} = 14$ nm/pulse, and at $T = 1050^\circ C$, $e^{PyC}_{1050} = 3$ nm/pulse.

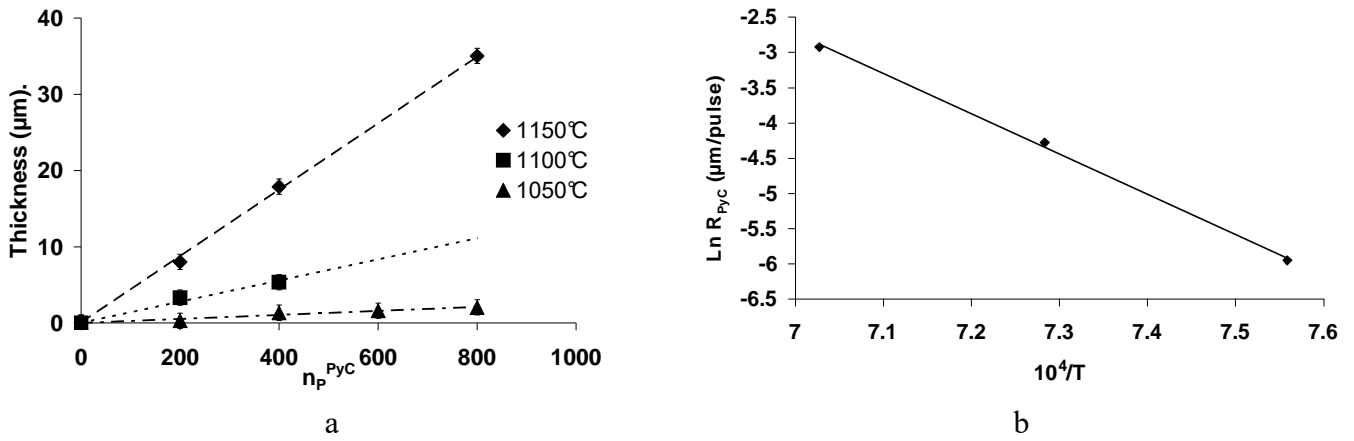


Figure 4a. Variations with the number of pulses of the PyC deposit thickness for various temperatures.

Figure 4b. Arrhenius plot of the PyC deposition process.

The deposition rates as a function of the reciprocal temperature (Arrhenius plot) are shown in figure 4b. The variation is linear suggesting that the deposition process is thermally activated with a corresponding value of the apparent activation energy E_a equal to 470 kJ.

Textural analysis was achieved using SEM, as a function of the temperature (Figure 5). At low temperature (1050°C) there is no evidence of layering whereas at higher temperatures (1100 and 1150°C) the stratification is well pronounced. The mechanical behaviour of CMCs is highly sensitive to the PyC interphase texture. The fibre/matrix bounding is expected to be weaker when PyC is well laminated.

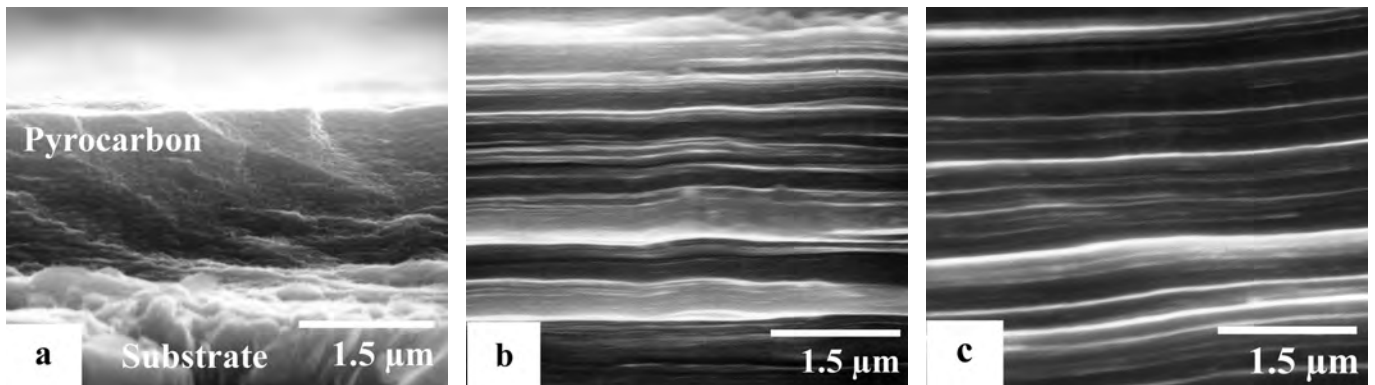


Figure 5. Textural evolution of a PyC deposit with temperature; (a) $T = 1050^\circ\text{C}$; (b) $T = 1100^\circ\text{C}$; (c) $T = 1150^\circ\text{C}$.

3.2 Thermodynamic calculations

The results of reaction (1) calculation are presented in table 1.

Table 1. Initial composition and result of the calculation for reaction (1).

Initial composition	Equilibrium composition
$\text{TiC}_{0.6}(\text{s}) = 10 \cdot 10^{-4} \text{ mol}$	$\text{TiC}_{0.949}(\text{s}) = 10 \cdot 10^{-4} \text{ mol}$
$\text{C}_3\text{H}_8(\text{g}) = 1.15 \cdot 10^{-4} \text{ mol}$	$\text{H}_2(\text{g}) = 4.66 \cdot 10^{-4} \text{ mol}$
	$\text{CH}_4(\text{g}) = 0.12 \cdot 10^{-6} \text{ mol}$

In the table (1), only the most important compounds in quantity are given at the equilibrium. Other compounds are found, but their quantity is negligible. From this calculation, the carbide becomes quasi-stoichiometric at the equilibrium (the carbon content increase from 37.5 at.% up to 48.7 at.%). From thermodynamic point of view, it is possible to increase the carbon content of a non-stoichiometric TiC by reaction of gaseous propane on solid non-stoichiometric titanium carbide during PyC deposition.

The results of reaction (2) calculation are presented in table 2.

Table 2. Initial composition and result of the calculation for reaction (2).

Initial composition	Equilibrium composition
$\text{TiC}_{0.974}(\text{s})=10 \cdot 10^{-4} \text{ mol}$	$\text{TiC}_{0.972}(\text{s})=10 \cdot 10^{-4} \text{ mol}$
$\text{TiCl}_4(\text{g})=1.91 \cdot 10^{-6} \text{ mol}$	$\text{H}_2(\text{g})=0.54 \cdot 10^{-4} \text{ mol}$
$\text{H}_2(\text{g})=1.14 \cdot 10^{-4} \text{ mol}$	$\text{HCl}(\text{g})=7.37 \cdot 10^{-6} \text{ mol}$
	$\text{TiCl}_3(\text{g})=7.23 \cdot 10^{-8} \text{ mol}$
	$\text{TiCl}_4(\text{g})=1.16 \cdot 10^{-8} \text{ mol}$
	$\text{CH}_4(\text{g})=7.97 \cdot 10^{-9} \text{ mol}$
	$\text{TiCl}_2(\text{g})=6.32 \cdot 10^{-10} \text{ mol}$

From this result, it does not seem possible to decrease significantly the carbon content of a bulk stoichiometric TiC by reaction between $\text{TiC}_{0.974}$ and TiCl_4/H_2 gas mixture. This result may be considered carefully because it does not take into account the carbon diffusion phenomenon through the stoichiometric TiC layer.

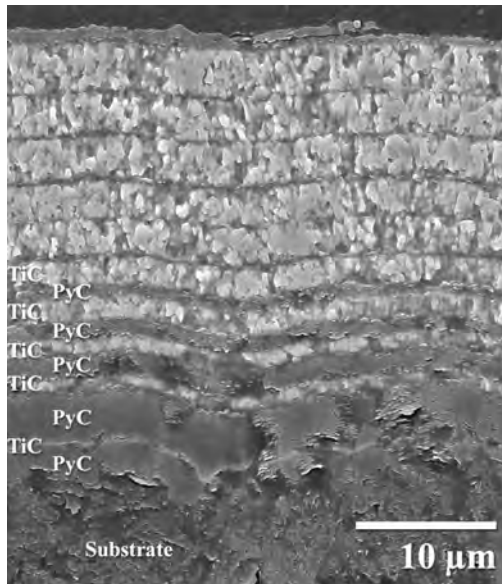
In the case of multilayered coatings, taken into consideration the previous thermodynamic calculations, the PyC deposit from propane onto a non-stoichiometric TiC pre-deposited may induce an increase of the carbon content in the carbide. This possibility is expected to have a strong influence on the layer interface bonding. Furthermore, as the TiC sublayer deposited is thin and between two PyC sublayers in our case, the carbide should be stoichiometric.

3.3 Processing of $(\text{PyC}/\text{TiC}_y)_n$ multilayered coatings

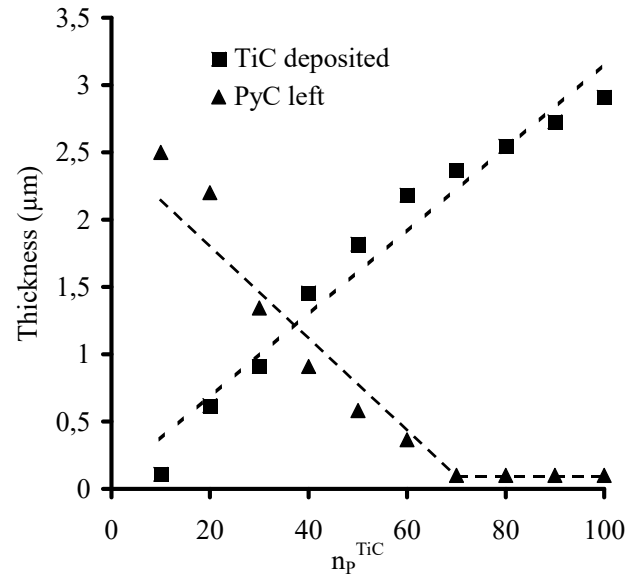
In order to process each TiC layers by RCVD from PyC sublayer consumption and to avoid any substrate influence, the first sublayer deposited on the substrate is PyC.

Figure 6a shows a SEM micrograph of a $(\text{PyC}/\text{TiC})_{10}$ multilayered deposit. In this case, a constant number of pulses for each PyC layer deposition ($n_p^{\text{PyC}}=10$) has been used, while a progressive one has been used for TiC layer deposits ($n_p^{\text{TiC}}=10, 20, 30, \dots, 100$). This micrograph shows the increasing thickness of TiC whereas the thickness of PyC sublayers decreases (with n_p^{PyC} constant).

Figure 6b represents the thickness evolutions e^{PyC} and e^{TiC} versus the number of pulses n_p^{TiC} extracted from SEM measurements. As n_p^{TiC} and e^{TiC} are increasing together, e^{PyC} is decreasing owing to the carbon consumption occurring during the P-RCVD carbide layer growth. The growth rate of TiC seems constant. Thus, the chemical reaction between carbon and TiCl_4/H_2 could be the limiting step. This feature is surprising for Vincent *et al.* have previously reported in isobaric RCVD a parabolic growth law owing to the limiting effect of carbon diffusion [11]. In order to explain this discrepancy, an assumption is based on a possible effect of the pulsed process itself, where the system is moving during the gas evacuation phase (t_e). Specific studies are in progress.



a



b

Figure 6a. Multilayered coating $(PyC/TiC)_{10}$, where $n_p^{PyC}=10$ and $n_p^{TiC}=10, 20, 30, \dots, 100$.

Figure 6b. Thickness of PyC and TiC sublayers versus n_p^{TiC} plot.

PyC seems totally consummated between the last TiC sublayers. Nevertheless, the TiC thickness still linearly increases. This feature suggests that carbon is also consummated far from adjacent sublayers.

In spite of the consumption of PyC layers, no "welding" phenomenon seems to occur. The last TiC sublayers remain well-separated from each other as observed in figure 7 where crack deflections are shown at TiC/TiC interfaces.

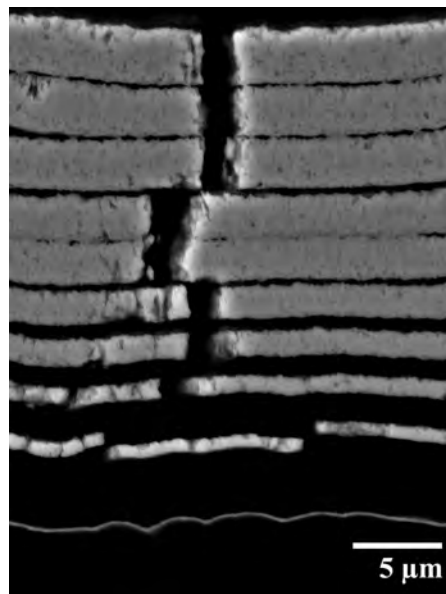


Figure 7. SEM observation of the multilayered $(PyC/TiC)_{10}$ showing crack deflections.

3.4 Mechanical behaviour of carbon fibres with $(PyC/TiC)_n$ multilayered coatings

A sub-micrometric multilayered coating $(TiC)_7$ has been deposited on carbon fibres with $n_p^{PyC}=1$ and $n_p^{TiC}=6$ per sublayer. The overall coating thickness measured by SEM is about 800 nm. SEM micrograph (figure 8a) clearly shows the different well separated layers.

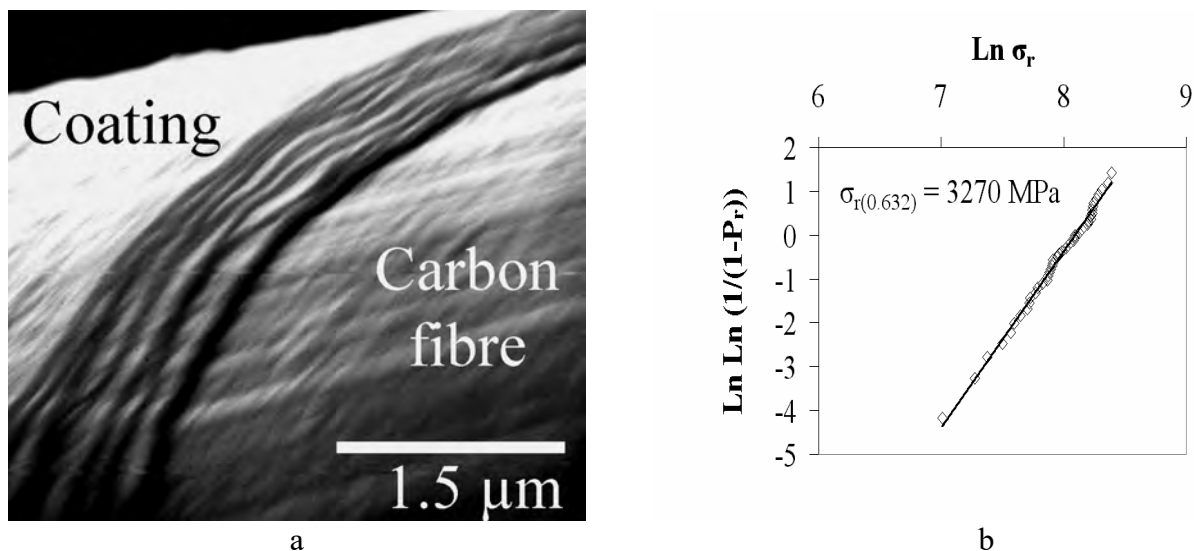


Figure 8. SEM micrograph of a carbon fibre coated with $(\text{TiC})_7$ (a) and Weibull statistic result (b).

These fibres exhibit a tensile strength $\sigma_{r(0.632)}$ equal to 3270 MPa (figure 8b). In a first estimation, with respect to the uncoated fibre, the presence of the coating does not imply a significant decrease of the mechanical properties of the coated fibre ($\sigma_{r(0.632)} = 3270$ MPa for the coated fibres versus $\sigma_{r(0.632)} = 3575$ MPa for the uncoated ones). The as-coated fibres keep a sufficient tensile strength for being used as reinforcement in CMCs.

4. CONCLUSION

$(\text{PyC}/\text{TiC})_n$ multilayered deposits have been processed by P-RCVD on plane substrates. Pyrocarbon consumption and carbon diffusion through the carbide layers are responsible for the TiC growth mechanism and the resulting PyC layer thickness. From thermodynamic calculations, the thin carbide sublayers should be stoichiometric. The combination of P-CVD and P-RCVD allows a sharp control of each sublayer thickness. Furthermore, it seems possible to consume the PyC intercalated between adjacent carbide sublayers.

This method has been achieved to fibre coating. The very first mechanical tests carried out on coated fibres are encouraging. The next step of this work lies in the study of such coatings as interphases in CMCs.

References

- [1] Naslain R., Composite Interfaces, **1** [3] (1983) 253-286.
- [2] Evans A. G., Zock F. W., J. Mater. Sci., **29** (1994) 3857-3896.
- [3] Bertrand S., Forio P., Pailler R., Lamon J., J. Am. Ceram. Soc., **82** [9] (1999) 2465-2473.
- [4] Bouix J., Vincent C., Vincent H., Favre R., Mat. Res. Soc. Symp. Proc., **168** (1990) 305-310.
- [5] Bouix J., Berthet M. P., Bosselet F., Favre R., Peronnet M., Rapaud O., Viala J. C., Vincent C., Vincent H., Comp. Sci. And Technol., **61** (2001) 355-362.
- [6] Dupel P., Pailler R., Langlais F., J. Mater. Sci., **29** (1994) 1341-1347.
- [7] Van Loo F. J. J., Bastin G. F., Metall. Trans. A, **20A** (1989) 403-411.
- [8] Vincent C., Dazord J., Vincent H., Bouix J., J. Crystal Growth, **96** (1989) 871-880.
- [9] Langlois R., J. Mater. Sci. Lett., **10** (1991) 1049-1051.
- [10] Patankar S. N., J. Mater. Sci. Lett., **10** (1991) 1176-1181.
- [11] Vincent C., Dazord J., Vincent H., Bouix J., Thermochim. Acta, **138** (1989) 81-96.