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Reactive Chemical Vapour Deposition of titanium carbide from H$_2$-TiCl$_4$ gas mixture on pyrocarbon: A comprehensive study

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Abstract

In Reactive Chemical Vapour Deposition (RCVD), the absence of one element of the deposited carbide in the initial gas phase involves the consumption/conversion of the solid substrate. In this way, the growth of a continuous carbide layer on the substrate requires solid-phase diffusion of the reagent.

In this work, a parametric study of the RCVD of titanium carbide from pyrocarbon (PyC) and an H$_2$-TiCl$_4$ mixture has been carried out. Conversion ratio, PyC consumption and carbide layer growth kinetics have been determined at 1000°C. The influence of the H$_2$/TiCl$_4$ dilution ratio has been also investigated. The apparent inter-diffusion coefficient of the carbon through the TiC deposited layer and the direct apparent reaction rate were determined from a comparison between simulations based on a Deal-Grove-type model and the experimental results. The study has been completed with FTIR spectrometry analyses of the gases.

*Keywords*: CVD ; R-CVD ; TiC coating ; pyrocarbon ; solid state diffusion ; FTIR ; simulation

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Nomenclature	
k_d	Direct rate constant (mol.m^{-2}.s^{-1})
k_i	Inverse rate constant (mol.m^{-2}.s^{-1})
r	Dilution ratio of TiCl$_4$ in H$_2$
x	Carbon content in the TiC
D_C	Solid-state apparent inter-diffusion coefficient of carbon in TiC (m^2.s^{-1})
D_{TiCl4}	Gaseous diffusion coefficient of TiCl$_4$ (m^2.s^{-1})
$p_{TiCl4,s}$	TiCl$_4$ partial pressure on the deposition surface (Pa)
$p_{TiCl4,\infty}$	TiCl$_4$ partial pressure in the RCVD reactor (Pa)
$p_{H2,\infty}$	H$_2$ partial pressure in the RCVD reactor (Pa)
v_r	Reaction *(1)* rate (mol.m^{-2}.s^{-1})
j_C	Carbon flux from the PyC layer across the deposited TiC layer (mol.m^{-2}.s^{-1})
j_{TiCl4}	TiCl$_4$ flux from the bulk of the reactor across the limit diffusion layer (mol.m^{-2}.s^{-1})
$V_{m,C}$	Carbon molar volume (m^3.mol^{-1})
$V_{m,TiC}$	TiC molar volume (m^3.mol^{-1})
c_0	Reference concentration of the TiC (1/ $V_{m,TiC}$) (mol.m^{-3})
a_i	Interfacial activity of carbon (interface between TiC and PyC)
a_s	Carbon activity in the gas phase near the reaction surface
R	Perfect gas constant (J.mol^{-1}.K^{-1})
T	Temperature (K)
θ	Temperature (°C)
δ	Limit diffusion layer (m)
P_0	Reference pressure (Pa)
$R_{v,th}$	Theoretical conversion ratio
$R_{v,ap}$	Apparent conversion ratio
e_{TiC}	TiC thickness (meters for the modeling part and nanometers for the experimental part)
$e_{C,cons}$	PyC consumed thickness (nm)
$e_{C,ini}$	Initial PyC layer thickness (nm)
$e_{C,res}$	Residual PyC layer thickness (nm)

1. Introduction

Titanium carbide (TiC) is a frequently studied material for nuclear (Groot et al., 1991) and aerospace engineering applications (Boving and Hintermann, 1990). This material is extremely hard, has good corrosion resistance and refractoriness and is highly electrically conducting. These characteristics made him a good material for being studied.

The Reactive Chemical Vapour Deposition (RCVD) method is used to form carbide coatings and allows thin, homogeneous and adherent layers to be obtained. For instance, carbides (HfC, TiC ...) and boro-carbides (B$_4$C ...) from metals of groups 4 and 5 have been deposited for barrier applications in refractory ceramics (Piquero et al., 1995, Baklanova et al., 2006). These authors mentioned that RCVD coating are thin, homogeneous and adherent. The purpose of this work was to study the RCVD of titanium carbide from pyrocarbon according to the overall reaction *(1)*.

$$TiCl_{4(g)} + 2H_{2(g)} + C_{(s)} \overset{k_d}{\underset{k_i}{\rightleftarrows}} TiC_{(s)} + 4HCl_{(g)} \tag{1}$$
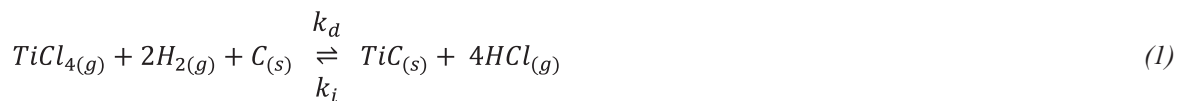
RCVD is based on the CVD principle with the main distinction that not all the elements of the deposited layer are present in the initial gas phase. This divergence between the two principles causes a main difference in the deposition mechanism which is the necessary solid-state diffusion of the element(s) from the substrate trough the deposited layer. So, the growth can be limited by this diffusion step.

The process was performed in two steps: the first was the pyrocarbon deposition, and the second was the RCVD treatment. In this work are reported the growth, consumption and conversion studies. The apparent inter-diffusion coefficient D_C of the carbon through the deposited TiC deposited layer was determined from a comparison between simulations based on a Deal-Grove-type model (Deal and Grove, 1965) and the experimental results. Reaction mechanisms were studied by FTIR analyses in several conditions.

2. Experimental

2.1. RCVD deposition procedure

In a first step, a highly anisotropic laminar pyrocarbon (PyC) pre-coating was deposited on initial substrates which were 1 cm diameter flat graphite cylinder. This deposited layer was performed in a vertical hot wall CVD reactor heated by an electrical resistance furnace. The deposition conditions were in accordance with those of Vallerot *et al.*, 2006. These pre-coatings have been made with three different durations to allow a better estimation of PyC consumption that occurs during the RCVD step. These conditions are presented in Table 1.

In a second step, the pre-coated samples were removed from the reactor for a vacuum heat-treatment in another furnace for one hour at 1500°C for restructuration and dehydrogenation of the PyC pre-coatings.

Table 1. Different coatings conditions (*standard cubic centimeter per minute)

Coatings type	Precursor	Temperature (°C)	Total flow rate (sccm)*	Residence time (s)	Deposition pressure (mbar)	Deposition durations	Dilution ratio (r)
PyC - CVD	C_3H_8	1000	300	0.5	30	1,2 and 3h	-
TiC - RCVD	$TiCl_4$-H_2	1000	300	0.5	50	30 to 300 min	3 and 10

In a final step, the pre-coated samples were replaced in the same CVD reactor than in the first step for the RCVD treatment itself with the deposition conditions presented in Table 1. For this work, the dilution ratio *r* was the parametric variable and is defined for the initial H_2-$TiCl_4$ gas mixture as presented in equation *(2)*.

$$r = \frac{[H_2]}{[TiCl_4]} = \frac{p_{H2,\infty}}{p_{TiCl_4,\infty}} \qquad (2)$$

In order to obtain several results from the same experimental run at different treatment times, a release system has been mounted in the reactor for the RCVD treatments. This system was made of internal and external magnets separated from each other by a quartz window placed at the top of the reactor at room temperature. It allowed the different samples hung to the internal magnets to be released one by one from the hot area down to a lower receptacle at 400°C. The TiC growth was thus quickly stopped and each dropped sample was retained in a non-oxidizing environment.

The layer thicknesses for different treatment durations allowed the determination of growth and consumption kinetics laws. These thicknesses were determined from SEM (Secondary Electron Microscopy) observation as
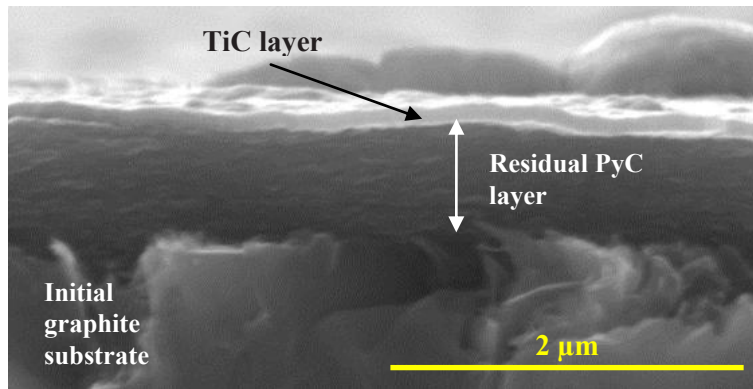
presented on Figure 1.

Figure 1. Fracture SEM micrography of TiC and residual PyC layers performed at 50 mbar and 1000°C after 4 hours of a RCVD treatment at R=10

2.2. Modeling

The determination of D_C has been made by the establishment of a unidirectional RCVD model. This model was based on assumptions similar to those of the Deal-Grove model (Deal and Grove, 1965), originally designed for the growth of a silica layer by oxidation of a silicon-containing substrate, and based on the dissolution and diffusion of oxygen in the silica layer from the surface to the interface. As in the Deal-Grove model, the growth process is followed beyond an initial transient and the mass fluxes through all layers are identical between themselves at all considered times. For this model, the deposition is based only on the chemical reaction *(1)*. The apparent diffusion coefficient of titanium in TiC is about 10^4 times lower than for carbon (Van Loo and Bastin, 1989); consequently, the reaction is assumed to be allowed only by carbon diffusion from the initial PyC substrate trough the growing TiC layer. So, the kinetics is driven by the outwards diffusion of carbon instead of the inwards diffusion of the reactant as in the Deal-Grove case.
The model features a three step mechanism for growth, as presented below:

    i)   The reactive gaseous species (assimilated to $TiCl_4(g)$ in regard of equation *(1)*) are transported from the bulk gas to the outer TiC surface where they are adsorbed;

    ii)   Carbon diffuses across the TiC layer from the solid carbon layer towards the outer TiC surface;

    iii)   Carbon and adsorbed gaseous species react to form the new TiC layer

In the case of a sufficient renewal of the atmosphere, which could be a good hypothesis for a CVD process, the effect of HCl can be neglected and the reaction rate, calculated by equation *(3),* is equal to the inward $TiCl_4$ flux and to the outward carbon flux as described by equation *(4)*.

$$v_r = k_d a_s \frac{p_{TiCl_4,s}}{P_0} \tag{3}$$

$$v_r = j_C = -j_{TiCl_4} \tag{4}$$

Combining Fick's first law for carbon in TiC and for $TiCl_4$ in the gas phase to equations *(3)* and *(4)*, the

evolution of the chemical activity of carbon on the reaction surface is obtained, as related in equation *(5)*.

$$D_C . c_0 . \frac{a_i - a_s}{e_{TiC}} = \frac{k_d a_s}{P_0} \left(p_{TiCl_4,\infty} - \frac{D_C . c_0 . (a_i - a_s) RT\delta}{e_{TiC} D_{TiCl_4}} \right) \qquad (5)$$

The carbon activity in the gas phase near the deposition surface is not experimentally determinable. It is useful to have another equation describing the temporal thickness evolution during this deposition. The carbon flux determined for a stoichiometric conversion of carbon is presented on equation *(6)*.

$$j_C = c_0 \frac{de_{TiC}}{dt} \qquad (6)$$

This equation combined with equations *(3)* and *(4)* yield equation *(7)*, giving the evolution of the thickness with the RCVD processing time.

$$\frac{de_{TiC}}{dt} = V_{m,TiC} . D_C . c_0 . \frac{a_i - a_s}{e_{TiC}} \qquad (7)$$

To conclude, the RCVD model developed for the deposition of TiC from carbon is a simultaneous resolution of the algebraic equation *(5)* and of the differential equation *(7)*.

2.3. RCVD reaction study

For a better understanding of the chemical mechanism, the solid condensed on the outlet reactor cold parts and the gas phase were studied by Fourier Transform Infra-Red spectroscopy (FTIR). This study was performed in a second low pressure hot-wall CVD reactor that was smaller in size and coupled with the FTIR spectrometer as described in the previous works of Langlais *et al.*, 2005.
Two types of analyses were performed:
- *In-situ* and *ex-situ* analyses without substrate for homogeneous gas phase reactions studies
- *Ex-situ* 60-minute analyses with high specific surface area substrates to enhance the heterogeneous reactions that can produce carbon-containing gaseous species.

The *ex-situ* analyses were performed in an external column analysis cell where the cold reacted gas mixture was guided. The IR signal was directed in this analysis cell by mirrors and IR-transparent windows from the spectrometer to the analyzer. *In-situ* analyses were performed in a similar fashion directly inside the CVD reactor. The substrates used for some IR analyses were Aiguitex® carbon fibre preforms of hollow cylindrical shape placed in the 2-3 cm-long hot area. These treatments were made at 1000°C and 50 mbar from the initial TiCl$_4$-H$_2$ gas mixture. The total gas flow rate was adjusted in order to keep a residence time of 0.5 s.

3. Results and discussion

At first approximation, the RCVD growth of TiC is described by the global reaction *(1)*. The deposition process could be presented like a total conversion of PyC into TiC. In this case, the theoretical volume conversion ratio $R_{v,th}$ is determined by equation *(8)* where $V_{m,TiCx}$ is the molar volume of TiC$_x$ determined by considering the lattice parameter variation of TiC$_x$ with the carbon content "*x*" (<1) (Hanabusa, 1999).

$$R_{v,th} = \frac{V_{m,TiCx}}{x \cdot V_{m,C}} \tag{8}$$

The theoretical evolution of the conversion ratio is presented in Figure 2 and shows that the minimal value of $R_{v,th}$ is obtained for nearly stoichiometric TiC.

With results of about 30 thickness values measured for each processing time, the growth and associated PyC consumption are reported on Figure 3. PyC consumption is determined by equation *(9)*.
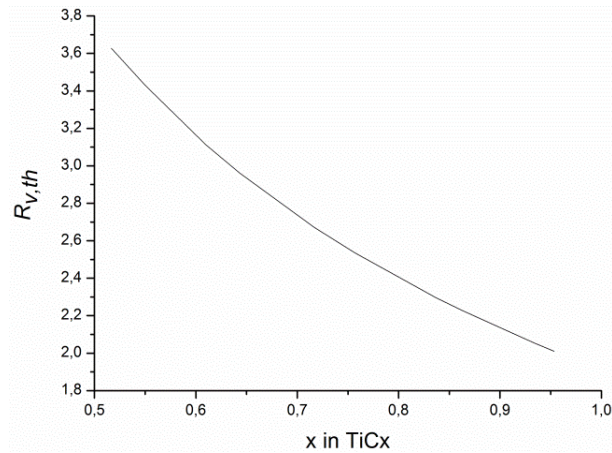
$$e_{C,cons} = e_{C,ini} - e_{C,res} \tag{9}$$

Figure 2.Theoretical evolution of the conversion ratio $R_{v,th}$ with the TiC carbon content
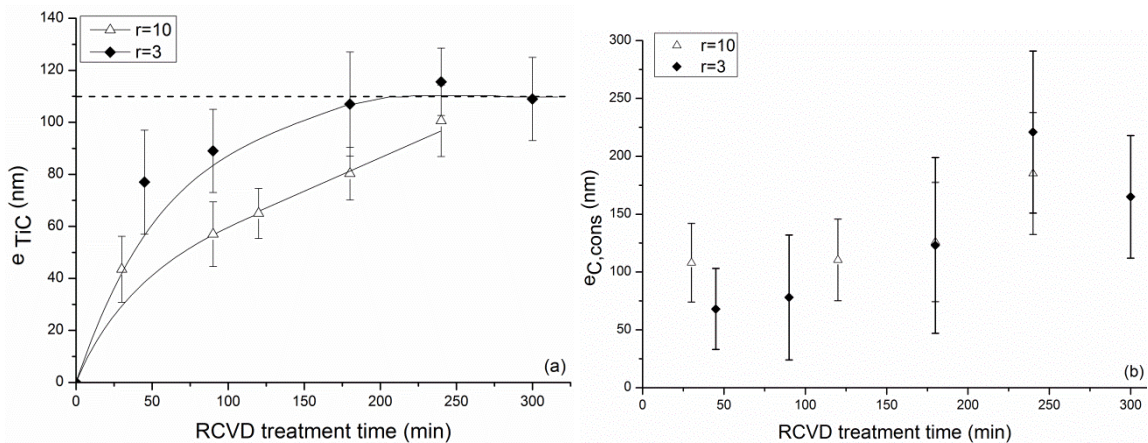

Figure 3. Experimental thicknesses evolution with RCVD treatment durations (a) TiC growth (b) PyC consumption

The kinetics depends on the dilution ratio *r* for the first 0-200 min time period in which the growth rate is higher with *r*=3 than with *r*=10 (Figure 3.a). For *r*=3, after these durations, the deposition seems to stop and the layer thickness seems to be limited to about 110 nm. A results which cannot be extend to the kinetic at *r*=10. However, despite the significant uncertainties due to measurement difficulties, the evolution of the consumed PyC thickness $e_{C,cons}$ shows, like for the TiC grown thickness e_{TiC}, an increase of the PyC layer

consumption $e_{C,cons}$ with the RCVD treatment duration (Figure 3.b).

$$R_{v,ap} = \frac{e_{TiC}}{e_{C,cons}} \qquad (10)$$

The average apparent conversion ratio $R_{v,ap}$ calculated by equation *(10)* from the different experiments is about 0.7, so clearly below the minimal value of $R_{v,th}$ even taking into account the uncertainties. The thinness of the measured layers measured and the penetration of the electron beam used for atomic analyses like electron-microprobe analyses did not permit the stoichiometry measurement of the TiC layer. Whatever the TiC stoichiometry, the low measured $R_{v,ap}$ evidences that the consumed carbon is not only involved in the growth of the TiC layers according to overall reaction *(1)*, but also in another reaction yielding gaseous carbonaceous by-products which are transported away from the reactor area.
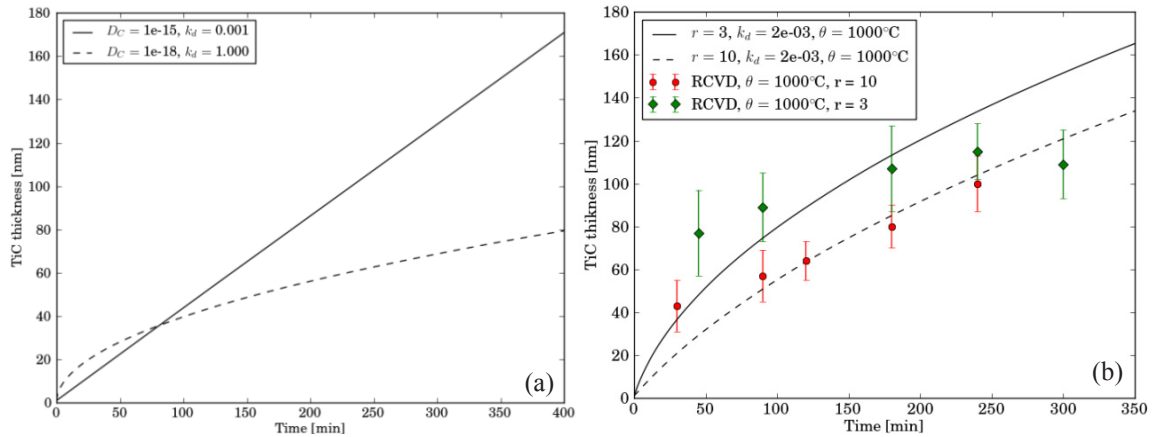

Figure 4. Simulations based on a Deal-Grove-type model for the TiC deposition from carbon and TiCl$_4$-H$_2$ gas mixture at 1000°C and r=10 for different possible regimes (a) and fitting results for $D_C = 3\times10^{-18}$ m^2.s^{-1} and $k_d = 2\times10^{-3}$ mol.m^{-2}.s^{-1} (b)

The experimental data points have been fitted by model curves through the optimization of two model parameters: the carbon diffusion coefficient D_C and the surface direct reaction rate constant k_d. In the model, two main growth regimes can take place. The first one is a reaction-limited regime as presented by the solid straight line in Figure 4.a: the growth rate is constant and depends only on the direct apparent reaction rate k_d and on the dilution ratio r. This regime is encountered for low values of k_d and high values of D_C/e_{TiC}. The second one is a solid-state diffusion limited regime as illustrated by the dashed parabolic curve in Figure 4.a; the growth rate depends heavily on D_C and little on r. This regime is encountered for high k_d values and low D_C/e_{TiC} values. The model used does not account for the apparent growth ending observed for long RCVD treatment durations.

For both r values, the best fit between the simulated curves and the experimental data is obtained with $D_C = (3\pm0.5)\times10^{-18}$ m^2.s^{-1} and k_d around 2×10^{-3} mol.m^{-2}.s^{-1}. Because the TiC growth rate is both decreasing over duration and dependent on r, it can be concluded that growth occurs in the area of transition between the two regimes described above. As in the study of Fakih *et al.*, 2008, on the RCVD TiC growth from SiC at 1100°C, the D_C value obtained for RCVD is two orders of magnitude higher than that obtained from the data by Van Loo and Bastin, 1989, who used a diffusion couple technique. According to Fakih *et al.*, 2008, the discrepancy is likely due to the difference in carbide grain size: sub-micrometric in the RCVD case versus several tens of microns in the diffusion couple technique case.

FTIR analyses were performed to detect the different species including the possible carbon-containing ones produced in the gas phase during the reaction. The IR spectra are presented in Figure 5. For *ex-situ* analyses without substrate, the spectrum obtained for the initial $TiCl_4$-H_2 cold mixture is similar to the one obtained after flowing through the hot area heated at 1000°C. These spectra are in accordance with precedent IR-analyses of $TiCl_4$ realised by Johannesen *et al.*, 1954. In the same conditions, *in-situ* analyses showed however the appearance of bands at 810 and 830 cm^{-1} and an increase of the intensity of the band at 905 cm^{-1}. These bands could not be currently assigned but further investigations are in progress in a larger spectral range notably with commercial titanium subchlorides for comparison.

In the absence of substrate, the produced species are few in quantity and most of them condense on the cold parts before reaching the analysis cell installed at the reactor outlet for *ex-situ* analyses which explains that they are observed only by *in-situ* analyses. The addition of a high specific surface carbon substrate results in the increase of the intensities of these bands by exacerbating the RCVD reaction. Additional bands are shown at 1097 and 1263 cm^{-1}. The band at 1263 cm^{-1} could be assigned to symmetric bending vibrations ($\delta_s CH_3 + \delta_s TiCl_3$) at 1267 cm^{-1} for $CH_3 TiCl_3$ as in the gas analyses of Mc Kean *et al.*, 1991 and ($\delta_s CH_3$ + an harmonic at 152 cm^{-1}) at 1273 cm^{-1} for $(CH_3)_2 TiCl_2$ calculated by McGrady *et al.*, 1997. The band at 1097 cm^{-1} could also be assigned to a symmetric bending vibration ($\delta_s CH_3$) present at 1092 cm^{-1} in the $CH_3 TiCl_3$ as in the solid analyses of Mc Kean *et al.*, 1991 and to the harmonic of the asymmetric stretching vibration ($2 \times \upsilon_{as} TiC_2$) at 1086 cm^{-1} for $(CH_3)_2 TiCl_2$ calculated by McGrady *et al.*, 1997. However, the absence of the asymmetric bending vibration ($\delta_{as} CH_3$) at 1370-1375 cm^{-1} for these two molecules in spectra presented on Figure 5 does not permit to confirm the nature of the molecules present in these present analyses.

The hypothesis of the presence of such molecules could explain the overconsumption of the initial PyC layer observed during the growth of TiC. It is worthy of note that for *ex-situ* 60-minute analyses with a high specific surface area substrate a residual solid was deposited on the IR transparent cold window of the analysis cell. So in this last case, the spectrum includes the bands of the solids species in addition to the gaseous ones. The spectrum of the residual solid alone was obtained by vacuum purge of the analysis cell. Same but broader bands, typical of condensation, are found. Further work is in progress to confirm the assignment of the different IR bands.
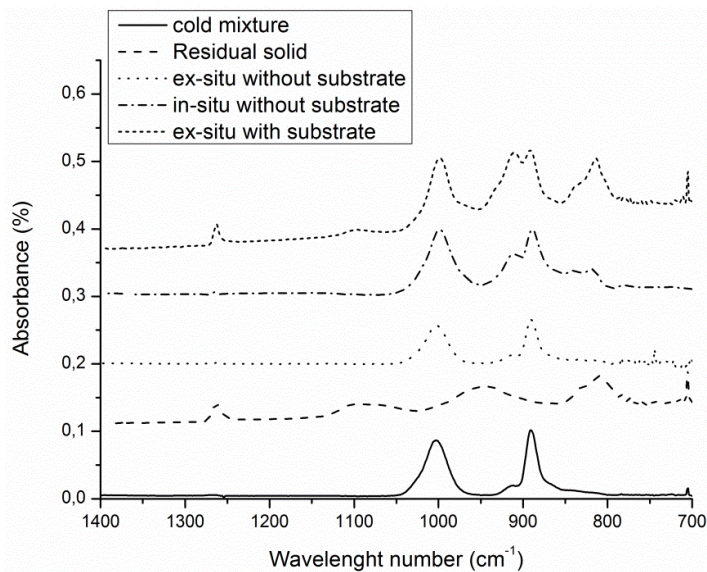

Figure 5. FTIR spectra of the gas and the residual solid deposited on the IR transparent cold window obtained in different conditions.

4. Conclusion

This work indicates a more complex mechanism than the simple reaction *(1)*. An overconsumption of the carbon substrate is evidenced during the RCVD process. The FTIR analyses seem to show the production of carbon-containing species in accordance with the observed carbon loss. The modification of the initial gas phase during its transport through the reactor to the deposition surface could also indicate the presence of intermediate species such as titanium sub-chlorides which can be the actual precursors for the reaction. The apparent inter-diffusion coefficient D_C of carbon through the TiC layer deposited at 1000°C determined from a simulation based on a Deal-Grove-type model, as well as the growth regime must be confirmed by further experimental results.

5. Acknowledgements

6. References

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