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CVD OF TITANIUM CARBIDE AT MODERATE TEMPERATURE FROM TITANIUM SUBCHLORIDES

B. DROUIN-LADOUCE, J.P. PITON\* and L. VANDENBULCKE

*Centre de Recherches sur la Chimie de la Combustion et des Hautes  
Températures, CNRS, F-45071 Orléans Cedex 2, France*

*\*Université d'Orléans, U.F.R. Faculté des Sciences, BP. 6759, F-45067  
Orléans Cedex 2, France*

**Résumé :** La formation in-situ des sous-halogénures de titane par réduction du tétrachlorure de titane par le titane métallique est utilisée conjointement avec du butane pour déposer des couches de carbure de titane à température modérée, de l'ordre de 850°C.

La vitesse de dépôt, la composition en C/Ti et en chlore des revêtements ainsi que leur microdureté sont étudiées en fonction des paramètres expérimentaux, spécialement la composition initiale de la phase gazeuse. En les comparant aux résultats de calculs thermodynamiques, les variations de la vitesse de dépôt et de la composition du solide permettent de discuter l'influence de différentes limitations cinétiques du processus qui interviennent en fonction des conditions de dépôt. Dans tous les cas un grand écart à l'équilibre est observé. On montre que ces conditions de température de dépôt modérée et de sursaturation élevée conduisent à une structure à grains très fins.

La microdureté des dépôts varie dans un large domaine. Des valeurs aussi faibles que 1000 kg.mm<sup>-2</sup> sont obtenues quand la quantité de chlore incorporée est élevée. Dans les meilleures conditions de dépôt, les couches sont bien cristallisées avec une concentration en chlore faible et un rapport C/Ti proche de 1. Dans ce cas la taille des grains est particulièrement plus faible comparée à celle observée sur les couches déposées de façon classique à température plus élevée, comprise entre 1000 et 1050°C, la morphologie est très dense et la microdureté atteint des valeurs entre 4000 et 5000 kg.mm<sup>-2</sup> sous une charge de 50g.

**Abstract :** The in-situ formation of the titanium subchlorides by the reduction of titanium tetrachloride by titanium metal is used together with butane to deposit titanium carbide layers at moderate temperature, in the order of 850°C.

The deposition rate, the C/Ti composition of the coatings, the chlorine incorporation and the microhardness are studied as functions of the initial gaseous composition. When compared with the thermodynamical calculations, the variations of the deposition rate and the solid composition allow to discuss the influence of different kinetic limitations of the process which arise as a function of the deposition conditions. In any case a great departure from the equilibrium is observed. It is shown that these conditions of moderate temperature and supersaturation lead to a very fine-grained structure.

The microhardness of the deposits varies in a large range. Values as low as 1000 kg.mm<sup>-2</sup> can be observed when the chlorine content is high. With the best deposition conditions, the deposits are well-crystallized with a low chlorine content and a C/Ti ratio approaching 1. In that case it is shown that the grain size is particularly lower than those observed in layers deposited at classical higher temperatures of 1000-1050°C, the morphology is very dense and the microhardness is in the range 4000-5000 kg.mm<sup>-2</sup> under 50g load.

### I Introduction :

In a previous study (1) a comparison between thermodynamic calculations applied to stoichiometric titanium carbide and some preliminary experiments for two systems TiCl<sub>4</sub> - C<sub>4</sub>H<sub>10</sub> - H<sub>2</sub> - Zn vapor and TiCl<sub>x</sub> - C<sub>4</sub>H<sub>10</sub> - H<sub>2</sub> (with x < 4) allowed to reveal the conditions necessary to overcome the kinetic limitations of the actual TiCl<sub>4</sub> - CH<sub>4</sub> - H<sub>2</sub> reactant gas mixture when

employed at moderate temperature. The role of  $TiCl_2$  through its reduction or its disproportionation was especially emphasized and it was shown that a prereducing step of  $TiCl_4$  to its subchlorides by elemental titanium coupled with the use of a less stable hydrocarbon like butane was an interesting way to decrease the deposition temperature of titanium carbide.

Thermodynamic calculations are extended here to non-stoichiometric titanium carbide and a more extensive experimental work is reported with the  $TiCl_x - C_4H_{10} - H_2$  system at  $850^\circ C$ . As a result from a comparison, the deposition mechanism is discussed and the deposition process optimized.

## II Experimental techniques :

The deposition apparatus presents some distinctive characteristics necessary to implement the process. It is composed of a hot-wall reactor ( of 53 mm ID ) surrounded by a two zones furnace. The first zone permits reducing  $TiCl_4$  by Ti curled chips at a higher temperature than deposition. Most of the hydrogen flow and the butane are introduced downstream in a colder part of the reactor while the  $TiCl_4$  is passing through the titanium chips in order to make up the whole mixture of hydrogen, butane and titanium chlorides which reacts in the deposition zone.

All the other parts are classical with a control unit of gas flow,  $TiCl_4$  evaporation and regulation of pressure. A pumping system carries the gases through a filter and various traps.

The following deposition conditions were used : deposition temperature =  $850 \pm 10^\circ C$ , Ti chips temperature =  $1050^\circ C$ , total pressure = 40 torr (  $5.33 \cdot 10^3$  Pa ), temperature of the  $TiCl_4$  evaporator =  $37^\circ C$ , butane flow rate =  $5-50 \text{ cm}^3/\text{mn}$ ,  $TiCl_4$  flow rate =  $5-50 \text{ cm}^3/\text{mn}$ , hydrogen flow rate through the  $TiCl_4$  evaporator =  $5-100 \text{ cm}^3/\text{mn}$ , total hydrogen flow rate =  $1000-4000 \text{ cm}^3/\text{mn}$ , deposition time  $\leq 2$  hours.

Most of the deposition experiments were carried out on steels samples, especially on XC 38 and Z220 CW 14, but cemented carbides were also tested as substrates. The growth rates of the coating were deduced from the mass increase per unit surface, generally during two hours, and the coating thicknesses were also measured on polished cross sections of the samples.

Fractured cross-sections were observed by S.E.M. and the chemical composition of the deposits were measured by quantitative microprobe analysis. Vickers microhardnesses of sufficiently thick coatings were measured under a 50g load.

## III Thermodynamical study :

### Generalities on the calculation procedure :

The chemical equilibrium calculations involve the minimization of the total Gibbs free energy taking into account the conservation of the mass of each element, a constant temperature and a constant total pressure. A slightly modified version of SOLGASMIX program elaborated by G. ERIKSSON (2) has been employed to perform the calculations of this paper. In this program, non-stoichiometric solids can be considered.

As reported previously (1) these calculations are common for all aliphatic saturated hydrocarbons as the C/H ratio is constant whatever n in the  $C_nH_{2n+2} + H_2$  mixture for a constant total pressure, a given titanium chloride concentration and an initial carbon concentration :  $n \cdot X^\circ C_nH_{2n+2}$ .

The following species were considered :  $H_2$ ,  $CH_4$ ,  $TiCl_4$ ,  $TiCl_3$ ,  $TiCl_2$ ,  $TiCl$ ,  $HCl$ ,  $Cl_2$ ,  $C_2H_2$  and  $CCl_4$  as constituents of the gaseous mixture;  $Ti_3C$  and  $TiC_x$  as solids ( pure Ti was considered as the solubility of C in Ti is low (3)).  $TiCl_2$  and  $TiCl_3$  solids were not taken into account as stoichiometric thermodynamical calculations showed that they were never produced at the conditions studied, especially when the partial pressure of these species were maximum, when  $a_{Ti} = 1$ .

All the thermodynamical properties of the gaseous species were taken in the JANAF tables. For non-stoichiometric solids, other data sources must be used. Several studies have reported thermodynamic properties of the  $TiC_x$  over its homogeneity range at temperature between 850 and 1900 K (3-5). The partial molar free energies of titanium were calculated at 1100 K from these results taking into account the free energy of stoichiometric TiC formation given by JANAF tables and the extent of the homogeneity range of the titanium carbide phase at 1100 K.

The carbon partial thermodynamic properties were deduced from the Gibbs-Duhem equation and the values of the titanium partial thermodynamic properties at 1100 K. The results have been compiled in a polynomial form disclosing the logarithm of the activity coefficients as a function of the composition.

At 1100 K the homogeneity range extends from C/Ti = 0.59 to C/Ti = 0.98 (3-6). For C/ti between 0.59 and 0.98 the following relations were used :

$$\ln \gamma_{Ti} = -233.585 + 116.509 X_{Ti} + 424.355 X_{Ti}^2 + 2712.417 X_{Ti}^3 - 3127.497 X_{Ti}^4 - 7095.273 X_{Ti}^5 + 8170.949 X_{Ti}^6$$

$$\ln \gamma_C = +57.935 - 206.835 X_C - 210.286 X_C^2 - 682.984 X_C^3 + 2807.068 X_C^4 + 3256.121 X_C^5 - 5829.924 X_C^6$$

were  $\gamma_i$  is the activity coefficient and  $X_i$  the molar fractions.

In the  $TiC_{0.98} + C$  two phases domain ( C/Ti  $\geq$  0.98) the C activity is equal to 1 and the Ti activity is constant and equal to its value in  $TiC_{0.98}$  that is :

$$a_{Ti} = 6.9427 \cdot 10^{-9} ; \gamma_{Ti} = 6.9427 \cdot 10^{-9} / X_{Ti}$$

In the  $TiC_{0.59} + Ti$  two phases domain ( C/Ti  $\leq$  0.59 ) the activity of Ti is supposed to be equal to 1 as the solubility of C in Ti is low (3) and the activity of carbon is constant and equal to its activity in  $TiC_{0.59}$  that is :

$$a_C = 1.31395 \cdot 10^{-10} ; \gamma_C = 1.31395 \cdot 10^{-10} / X_C$$

#### Calculation results :

From thermodynamic calculations of the interaction of  $TiCl_4$  with pure Ti at 1300 K, the C/Ti ratio was fixed at 3.0071. Then the equilibrium in the Ti - C - H - Cl system was calculated for different initial compositions in one mole of the  $TiCl_{3.0071} - C_4H_{10} - H_2$  gaseous mixture and constant values of the temperature and the pressure ( T = 1100 K and P =  $5.33 \cdot 10^3$  Pa ). In the following of this paper this  $TiCl_{3.0071}$  mixture of titanium chloride will be written  $TiCl_{3.0}$ .

Thermodynamic calculations are often used to specify the equilibrium domain of the different phases (  $TiC_x$ , Ti and C ) versus the initial gaseous mixture composition. When compared with the deposition domains calculated with  $TiCl_4$  (1), it is clear that the  $TiC_{0.59} + Ti$  deposition range is considerably enlarged especially at high  $X^\circ TiCl_{3.0}$ . On the other hand, the two phases  $TiC_{0.98} + C$  domain remains almost unchanged.

The variations in the production of the different gaseous species and solid phases are presented on fig.1 as a function of the initial gaseous composition. The theoretical efficiencies of Ti-containing species ( full lines ) and C-containing species ( dotted lines ) are plotted against  $4 X^\circ C_4H_{10}$  for a constant  $X^\circ TiCl_{3.0} = 2.8 \cdot 10^{-2}$ . The yields are defined with respect to  $X^\circ TiCl_{3.0}$  for Ti-containing species and  $4 X^\circ C_4H_{10}$  for C-containing species. As previously shown in the stoichiometric case (1),  $TiCl_3$  and  $TiCl_2$  have a high yield in the Ti-rich region despite the low temperature employed because  $TiCl_{3.0}$  chlorides were used as Ti-containing carriers in the initial mixture.

$TiCl_4$ ,  $TiCl_3$ ,  $TiCl_2$  efficiencies remains constant in the  $TiC_{0.59} + Ti$  domain as the Ti activity is equal to 1. Then  $TiCl_3$  and  $TiCl_2$  decrease quickly - especially  $TiCl_2$  - in the single phase region while the  $TiCl_4$  yield increases ( before it decreases also near the limit of the single-phase domain ). Thus as discussed previously from equilibrium calculations which involve stoichiometric TiC (1) this important amount of  $TiCl_4$  is produced by the disproportionation of the subchlorides. Accordingly, the subchlorides formed at 1300 K allow to liberate and incorporate Ti in a titanium carbide deposit at 1100 K.

The  $CH_4$  yield which is lower than  $10^{-6}$  in the two phases  $TiC_{0.59} + Ti$  domain and in the Ti-rich part of the single phase region increases quickly until it reaches a maximum value when the free carbon production begins. Then  $CH_4$  efficiency decreases as the free carbon yield rises.

The C/Ti variations are shown on fig.2 which presents the C.V.D. phase diagram for Ti-C solids deposited from  $TiCl_{3.0} - C_4H_{10} - H_2$  mixtures. While titanium carbide can be deposited

at equilibrium in a wide range of concentrations of the input reactants, this diagram shows the sensitivity of the composition of the non-stoichiometric titanium carbide phase to the initial mixture composition.

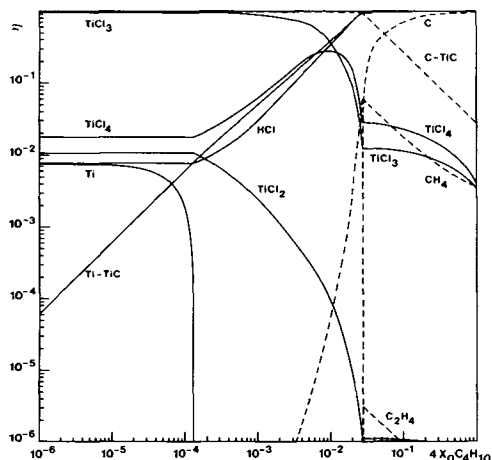


Figure 1: Variations of the equilibrium yields of the principal species as a function of the initial hydrocarbon content at  $X^{\circ} \text{TiCl}_{3,0} = 2,8 \cdot 10^{-2}$ ,  $T = 1100 \text{ K}$  and  $P = 5,33 \cdot 10^3 \text{ Pa}$ .

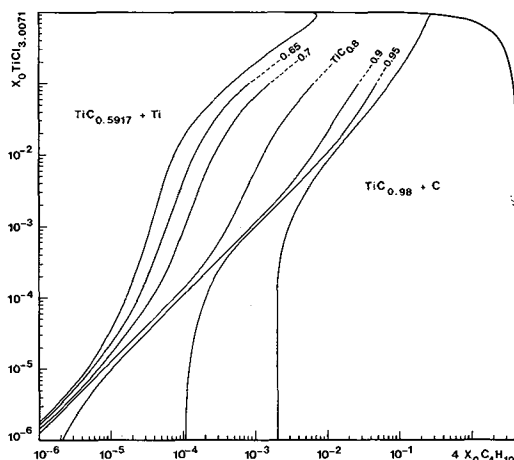


Figure 2: Phase fields for solid species and iso-concentration curves of titanium carbide in its single phase domain at equilibrium for  $\text{TiCl}_{3,0} - \text{C}_4\text{H}_{10} - \text{H}_2$  mixtures at  $T = 1100 \text{ K}$  and  $P = 5,33 \cdot 10^3 \text{ Pa}$ .

#### IV Comparison with the experimental results and discussion on the deposition mechanism :

The use of both a less stable hydrocarbon than methane and a prereducing step of titanium tetrachloride by titanium metal at a low pressure improves the chemical kinetics enough to allow the deposition of titanium carbide at a non-negligeable rate at moderate temperature. However some kinetics control of the process can occur again at these lower temperatures, producing some departure from the equilibrium. We remember that such kinetics control is in fact necessary to obtain nearly constant deposition conditions in large scale reactors. Two kinds of kinetics limitations can be considered, caused either by the reduction or (and) the disproportionation of the titanium subchlorides or by the pyrolysis of butane.

A comparison between the theoretical and the experimental C/Ti ratios versus  $4 X^{\circ} \text{C}_4\text{H}_{10}$ , at  $X^{\circ} \text{TiCl}_{3,0} = 2,8 \cdot 10^{-2}$ , is presented in figure 3. The corresponding variations of the theoretical yield and experimental growth rate are reported in figure 4 and all the experimental results are put together in figure 5, that is the variations of C/Ti, the growth rate, the chlorine incorporation and the microhardness of the deposits.

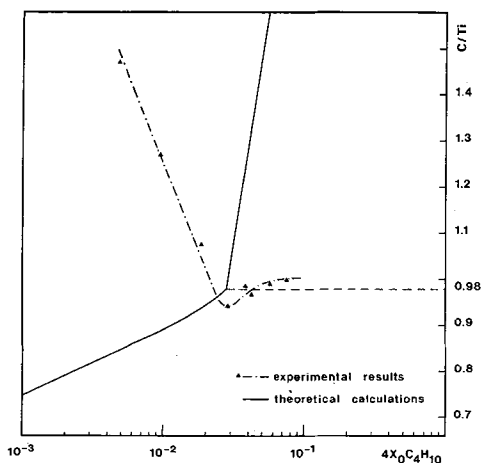


Figure 3 : Comparison of the variations of the C/Ti ratio between the equilibrium at  $T = 1100$  K and the experimental results at  $T = 1123$  K as a function of the initial hydrocarbon content for  $X^{\circ} TiCl_{3,0} = 2.8 \cdot 10^{-2}$  and  $P = 5.33 \cdot 10^3$  Pa.

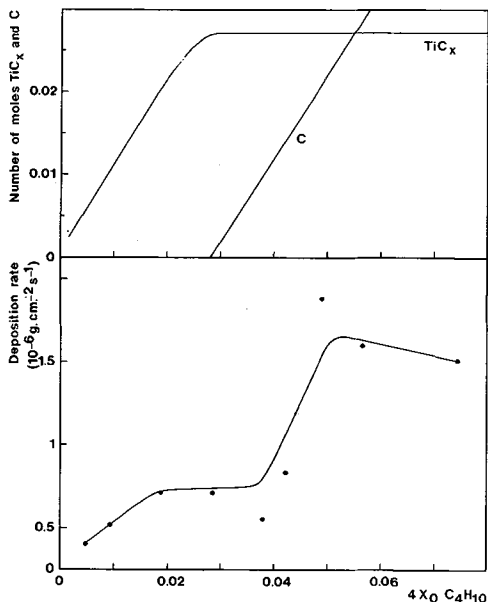


Figure 4 : Comparison between the yield of the solid species at equilibrium for one mole of initial mixture at  $T = 1100$  K and the deposition rate of the coatings deposited at  $T = 1123$  K versus the initial hydrocarbon content for  $X^{\circ} TiCl_{3,0} = 2.8 \cdot 10^{-2}$  and  $P = 5.33 \cdot 10^3$  Pa.

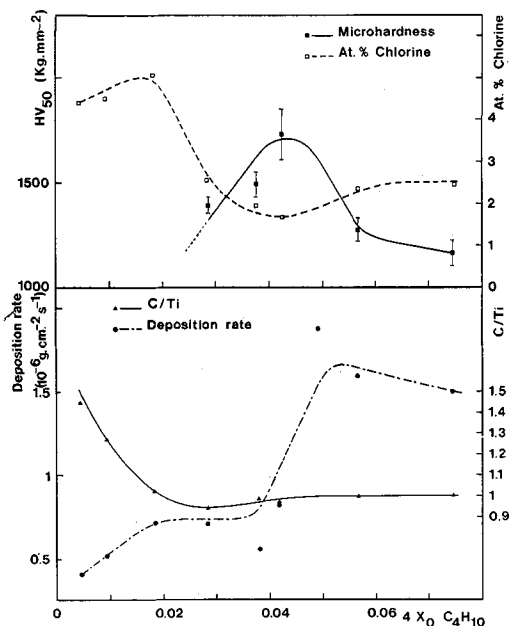


Figure 5 : Variations of the C/Ti ratio, the deposition rate, the chlorine content and the Vickers microhardness of the coatings deposited at  $X^{\circ} TiCl_{3,0} = 2.8 \cdot 10^{-2}$ ,  $T = 1123$  K and  $P = 5.33 \cdot 10^3$  Pa versus the initial butane concentration.

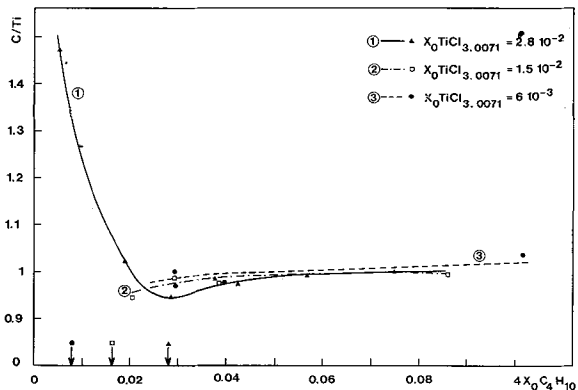


Figure 6 : Variations of the C/Ti ratio versus the initial hydrocarbon content for  $X^{\circ} TiCl_{3,0} = 2.8 \cdot 10^{-2}$ ,  $1.5 \cdot 10^{-2}$ ,  $6 \cdot 10^{-3}$  at  $T = 1123$  K and  $P = 5.33 \cdot 10^3$  Pa.

For  $4 X^\circ C_4H_{10} \leq 2.8 \cdot 10^{-2}$ , the experimental C/Ti ratio is far greater than the theoretical one (fig. 3) and free carbon has been detected by X-ray diffraction. In these conditions of high titanium subchlorides concentrations ( $X^\circ TiCl_{3.0} \geq 4 X^\circ C_4H_{10}$ ) titanium is not properly incorporated into the titanium carbide. Accordingly the chlorine content is very high in the corresponding region of figure 5. The whole results show some limitation of the process by the reduction and (or) disproportionation of the titanium subchlorides. This departure from equilibrium is apparently reduced for  $X^\circ TiCl_{3.0} = 4 X^\circ C_4H_{10}$  (fig. 3). However the similar theoretical and experimental values of C/Ti obtained for  $4 X^\circ C_4H_{10} = 2.8 \cdot 10^{-2}$  do not permit to conclude that near equilibrium conditions are reached because the experimental values afterwards vary only slightly up to about 1 when  $4 X^\circ C_4H_{10} \geq X^\circ TiCl_{3.0}$ .

Moreover microprobe analysis showed a C/Ti ratio near the stoichiometry and no free carbon has been detected by X-ray diffraction. The whole results obtained in this last range of the inlet composition depart a lot from the equilibrium results which predict an important deposition of free carbon (fig. 3-4). It is clear that, in this deposition range, the process is principally controlled by the decomposition of butane. Accordingly, the chlorine incorporation in the solid is lower as shown in figure 5.

A comparison, at  $X^\circ TiCl_{3.0} = 2.8 \cdot 10^{-2}$ , between the solid phases efficiencies at equilibrium and the experimental deposition rates (fig. 4) confirms the existence of the two kinetic controls. The coating rate variation exhibits two levels which can be linked respectively to the kinetics limitation of the titanium deposition and then the carbon incorporation when the ratio  $4 X^\circ C_4H_{10} / X^\circ TiCl_{3.0}$  increases.

It can be supposed that the kinetics limitation by the titanium incorporation rate is overcome because a transition occurs from a reduction reaction to a disproportionation one when  $4 X^\circ C_4H_{10}$  increases, as this second reaction type becomes thermodynamically enhanced in the single-phase deposition domain (fig. 1). Accordingly, the deposition rate increases for  $4 X^\circ C_4H_{10}$  in the range 0.04 - 0.05 until it is limited by the carbon incorporation (fig. 4). It is interesting to note that in that case the C/Ti ratio remains near the stoichiometric composition; when this limitation of the deposition rate is compared to the titanium carbide and free carbon yields predicted at equilibrium, it appears that high supersaturation in butane can be employed without deposition of free carbon. Such a result was previously reported also for the deposition of titanium carbide and boron carbide at higher temperature, respectively at about 1300 K and 1400 K when  $CH_4$  is employed as carbon containing specie (7,8). The inhibiting effect of  $CH_4$  reported previously (8) seems to be found again for  $C_4H_{10}$ , as the deposition rate slightly decreases for high values of  $4 X^\circ C_4H_{10}$ .

The figure 6 shows the variation of the experimental C/Ti ratio in the solid as a function of  $4 X^\circ C_4H_{10}$ , for three values of the inlet concentration of  $TiCl_{3.0}$ . When the concentration of  $TiCl_{3.0}$  decreases, the C/Ti ratio increases slightly for a constant concentration of  $C_4H_{10}$ , especially for  $4 X^\circ C_4H_{10}$  between 0.02 and 0.03. This result can be explained easily because the boundary between the single and two-phases domains occurs for decreasing values of the  $C_4H_{10}$  concentration when the  $TiCl_{3.0}$  concentration decreases (values of this limit are indicated by arrows in fig. 6). In any case, the important deposition of free carbon, predicted at equilibrium for  $C_4H_{10}$  concentrations higher than this limit, does not occur and an important departure from the equilibrium remains.

The figure 7 puts together the variations of the deposition rate, the composition of the solid (C/Ti and Cl content) and the microhardness as function of the  $TiCl_{3.0}$  concentration, for a constant value of  $4 X^\circ C_4H_{10}$  equal to  $3 \cdot 10^{-2}$ . According to fig. 6, the C/Ti ratio in the solid increases slightly as  $TiCl_{3.0}$  decreases. For  $X^\circ TiCl_{3.0}$  values lower than 0.01 it appears that the deposition rate is limited by the concentration of the titanium chlorides, and the chlorine content in the solid is low. As  $X^\circ TiCl_{3.0}$  increases, the deposition rate reaches a maximum and then slowly decreases: this result confirms the first level of figures 4 and 5 for the deposition rate, and corresponds to the kinetic limitation by the deposition rate of the titanium attributed to the reduction reaction. At the moderate temperature employed it is obvious that this leads to a higher incorporation of chlorine in the solid as shown on figure 7.

The influence of the initial conditions on the deposition mechanism will be more developed elsewhere (9).

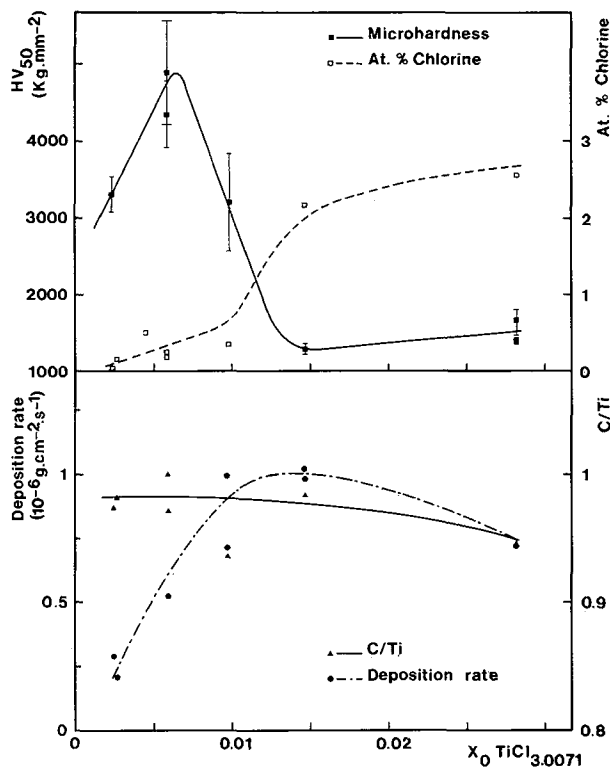


Figure 7 : Variations of the C/Ti ratio, the deposition rate, the chlorine content and the Vickers microhardness of the coatings deposited at  $4 X^{\circ} C_4H_{10} = 3. 10^{-2}$ ,  $T = 1123$  K and  $P = 5.33 10^3$  Pa versus the initial subchlorides mixture concentration.

#### V Optimization of the deposition process :

In order to improve the coating quality, the variations of the C/Ti ratio versus the inlet gaseous composition and the chlorine content in the solid, the deposition rate and the microhardness have to be compared to each other.

The existence of a certain chlorine amounts in the titanium carbide leads to a poor chemical stability and to poor coating properties. From figure 5, it is clear that the microhardness decreases when the Cl content increases for a nearly constant value of C/Ti, in the range 0.98 - 1 when  $4 X^{\circ} C_4H_{10}$  varies between  $3. 10^{-2}$  and  $8. 10^{-2}$ . The influence of the Cl content is confirmed by the figure 7, at least for  $X^{\circ} TiCl_{3.0} \geq 0.06$ . When its value is lower than 0.5 at.%, the microhardness does not depend a lot on the chlorine incorporated as shown on fig. 7 for  $X^{\circ} TiCl_{3.0} \leq 0.06$ . Hard titanium carbide deposits can therefore be deposited, as expected, if the Cl content is low and the composition near the stoichiometry. Such a result is obtained for  $X^{\circ} TiCl_{3.0} / X^{\circ} C_4H_{10} \leq 1$ , that is a ratio  $Ti/C \leq 1/4$  in the inlet gaseous mixture. Moreover the inlet Cl/H ratio must be sufficiently low to limit the chlorine incorporation but the deposition rate decreases at low reactant concentrations as shown on figure 7.

A compromise solution for the deposition at higher rate of a good deposit was found by increasing the titanium chloride and butane concentrations, the inlet ratio Ti/C being maintained equal or lower than 1/4. As the Cl content increases with  $X^{\circ} TiCl_{3.0}$  the threshold of 0.5 at.% Cl incorporated in the solid determines the upper limit of the  $TiCl_{3.0}$  concentration. Table I gives the results of some experiments carried out in this way, which leads to very high microhardnesses.



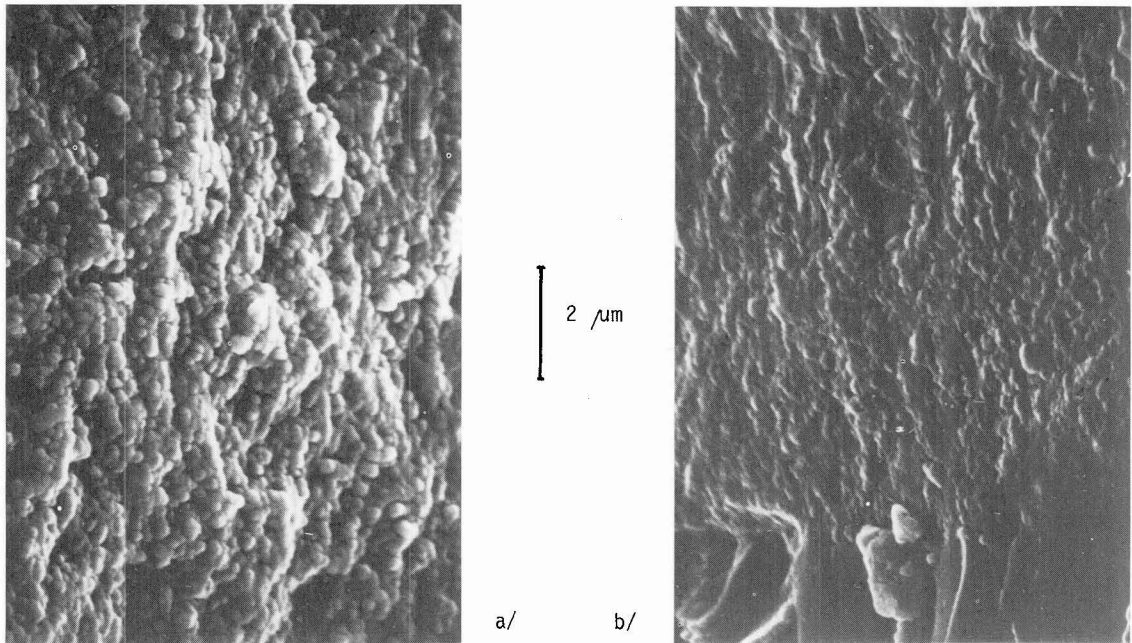


Figure 8 : S.E.M. micrograph of a fractured cross-section of a titanium carbide coating deposited on steel at moderate temperature a/ 1D23, b/ 1D39

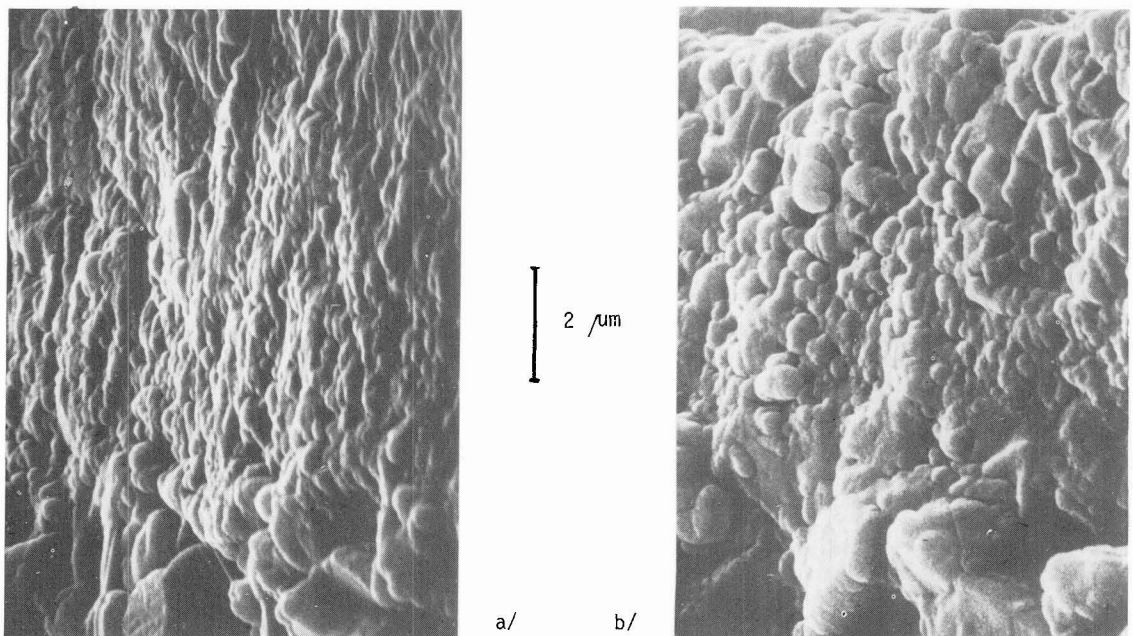


Figure 9 : S.E.M. micrograph of a fractured cross-section of a titanium carbide coating deposited on cemented carbide by a/ the moderate temperature process, b/ the classical C.V.D process.

TABLE I :

Sample number	X° TiCl <sub>3,0</sub>	4 X° C <sub>4</sub> H <sub>10</sub>	r*	Cl at.	C/Ti	Growth rate g.cm <sup>-2</sup> .s <sup>-1</sup>	Microhardness kg.mm <sup>-2</sup>
1D39	1.029 10 <sup>-2</sup>	5.791 10 <sup>-2</sup>	0.711	0.3 ± 0.02	0.96 ± 0.02	0.8	4950 ± 270
2D109	1.045 10 <sup>-2</sup>	5.795 10 <sup>-2</sup>	0.721	0.25 ± 0.03	0.98 ± 0.02	1.01	4800 ± 350
2D110	1.646 10 <sup>-2</sup>	8.522 10 <sup>-2</sup>	0.773	0.16 ± 0.10	0.99 ± 0.02	1.33	4800 ± 250

$$* r = X^\circ \text{TiCl}_{3,0} / X^\circ \text{C}_4\text{H}_{10}$$

TABLE II :

Sample number	X° TiCl <sub>3,0</sub>	4 X° C <sub>4</sub> H <sub>10</sub>	r*	Cl at.	C/Ti	Growth rate g.cm <sup>-2</sup> .s <sup>-1</sup>	Microhardness kg.mm <sup>-2</sup>
1D23	2.787 10 <sup>-2</sup>	7.431 10 <sup>-2</sup>	1.5	2.4 ± 0.27	0.99 ± 0.01	1.51	1160 ± 60
1D39	1.029 10 <sup>-2</sup>	5.791 10 <sup>-2</sup>	0.711	0.3 ± 0.02	0.96 ± 0.02	0.8	4950 ± 270

Values in the range 4700 - 5000 kg.mm<sup>-2</sup> were measured in samples coated at these special conditions (also for one experiment reported on figure 8) ; they are significantly higher than the classical reported microhardness of about 3200 kg.mm<sup>-2</sup> for TiC. Values in the range of 2600 - 3200 kg.mm<sup>-2</sup> were verified, with the same measurement conditions under 50g load, for layers deposited by the classical C.V.D process, from TiCl<sub>4</sub> - CH<sub>4</sub> - H<sub>2</sub> at T > 1000°C on cemented carbide.

These high values of the microhardness can be attributed to the grain refinement obtained with this process at moderate temperature, especially for the best conditions listed in the table I. The fractured cross-sections of two coatings deposited on steel in the conditions of table II are given on figure 8.

Sample N° 23 exhibits a quite fine grain but the Cl content is very high. Sample 1D39 was obtained within the range of conditions which optimize the composition of the solid and the grain refinement. It is interesting to note that the finest grain size which can be obtained depends on the substrate. As there is no difference in the growth rate of the TiC layer between steel and cemented carbide coated in the same conditions and as a decarburization interlayer has never been observed neither on steel nor on cemented carbide, the grain size variations could not be linked to the carbon diffusion from the substrate. On cemented carbides the grain size does not change a lot from the substrate to the surface (fig 9 a), but it is greater than on steel, and the best microhardnesses are lower, in the range 4000 - 4300 kg.mm<sup>-2</sup>, however the effect of constraints lower than on steel cannot be neglected. Figure 9 b presents for comparison a fracture of a TiC coating deposited on a cemented carbide by the classical C.V.D process.

Finer grain structures obtained in a single layer from this process at moderate temperature can be connected to the fine-grained structure achieved by the deposition of a multilayer coating and (or) the use of extraneous dopants in the deposition process at high temperature (10).

## VI Conclusion :

Titanium carbide coatings can be deposited at high rate, in the range 5 - 10 microns per hour, at a moderate temperature of about 850°C from butane instead of methane and a mixture of titanium chlorides prepared in-situ by the prereluction of the TiCl<sub>4</sub> by Ti metal.

From a comparison with a thermodynamic study, it can be shown that the deposition conditions and results deviate from equilibrium. The supersaturation at the deposit surface together with the moderate temperature lead to grain refinement. However, the final grain size depends to a certain extent on the substrate and its preparation. When associated with a low chlorine incorporation and a composition close to stoichiometry, the finest structure leads to a very high microhardness of 5000 kg.mm<sup>-2</sup>.

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