

Phase Equilibria and Reactive Chemical Vapor Deposition (RCVD) of Ti_3SiC_2

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The present article addresses the issue of properly modelling the thermodynamic aspect of chemical reactions proceeding at the solid/gas interface in a multi-component system. Attention is more especially paid to the formation of Ti_3SiC_2 by reactive chemical vapor deposition (RCVD) on a silicon carbide substrate heated at 1100 °C. A deposition diagram has been calculated by Gibbs free energy minimization in the C-Cl-H-Si-Ti quinary system. It is shown that this deposition diagram can account for experimental results obtained by RCVD only for the short period of time during which the reaction layer is thin and discontinuous. For thick, dense and continuous reaction layers, the deposition diagram is no longer appropriate and reaction-diffusion models developed for solid-state diffusion couples have to be used in place of it.

Keywords carbides, chemical potential gradients, diffusion paths, experimental study, local equilibrium, multicomponent diffusion, non-equilibrium processes

1. Introduction

Chemical vapor deposition (CVD) is a general surface coating process in which a reaction layer grows from a gas phase flowing at the surface of a solid substrate held at high temperature.^[1] In conventional CVD (CCVD), the hot substrate is chemically inert and species present in the coating are all coming from the gas phase. This is for example the case for the deposition of pyrolytic carbon layers from CH_4 ^[2] or of titanium carbide layers from $TiCl_4$ - CH_4 - H_2 mixtures.^[3] In reactive CVD (RCVD), the substrate plays an active part in the sense that a direct chemical reaction of at least one species present in it with the gas phase is a necessary condition for the coating to be grown. Many oxide, carbide, or nitride layers on refractory metals are produced by RCVD.^[4] A RCVD process has also been developed to coat the surface of carbon fibres with a carbide layer.^[5]

As other refractory MAX-phases, the ternary compound Ti_3SiC_2 (hexagonal symmetry, space group $P6_3/mmc$, $a = 0.3068$ nm, $c = 1.7669$ nm^[6]) possesses a set of mechanical properties of special interest for structural applications at high temperature.^[7,8] Owing to its ability to form kink bands and delamination cracks, this compound could more especially be used as an interphase deflecting microcracks in ceramic matrix composites. It is with this aim in view that thin layers of Ti_3SiC_2 were produced by

conventional CVD.^[9,10] However, the crystal size and orientation in the layers thus obtained were not satisfactory for interphase applications.^[9-11] A possible way for changing the microstructure of the deposited layer consists in using low gas pressure RCVD instead of conventional CVD, combined if necessary with pressure pulses.^[12,13] First attempts were thus made by reacting at 1100 °C a $SiCl_4 + H_2$ gaseous mixture with solid TiC: Ti_3SiC_2 was obtained in this way but difficultly and co-deposition of silicon carbide SiC was unavoidable.^[13] Layered structures containing Ti_3SiC_2 were easier to produce by reaction of a $TiCl_4 + H_2$ gas mixture with solid SiC at 1100 °C.^[14]

The present work is focused on the latter RCVD procedure. Attention will be paid to the relationships between the layer constitution and the phase equilibria in the Cl-H-C-Si-Ti quinary system. The objective is to achieve proper modelling of the chemical reactivity in the system, an approach that should be useful from an applied standpoint for optimizing both the deposition process and the coating properties.

2. Thermodynamic Analysis

As a general rule, the thermodynamic approach of a CVD process consists in establishing a “deposition diagram” from thermodynamic calculations based on Gibbs free energy minimization. This diagram gives the nature of the solid phases that are likely to be deposited from the gas phase at a given temperature and a given pressure as a function of gas composition. Many calculated deposition diagrams can be found in the literature as for example in references.^[2,3,10,13-16]

Three different processes are generally distinguished in Conventional CVD.^[1] These are: (i) the transport of reacting species by the flowing gas, (ii) the gas phase diffusion of these species through a boundary layer adjacent to the surface coating, and (iii) the development at the surface of the coating of chemical reactions including adsorption,

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nucleation, surface migration, and desorption. In the calculation of any deposition diagram, it is assumed that “close to equilibrium conditions” tend to be established at the solid/gas interface. It can reasonably be assumed that the best situation to fulfil these conditions is when chemical reactions proceed at a fast rate compared with gas phase transport and diffusion. Practically, this situation occurs when the growth of the CCVD coating is controlled by the rate at which the gaseous species are brought to the deposition zone. From statistical probability considerations, it should take a shorter time to build a crystal by surface reactions with one type of atom than with two, three, or more types. Therefore as the number of different atoms increases, the probability that surface reactions become rate limiting also increases. Consequently, fulfilling the “close to equilibrium conditions” should be easier for elements and binary compounds than for ternary ones. As a matter of fact, experimental results and calculated deposition diagrams are often in very good agreement for elements or binary compounds deposited by CCVD, provided that reliable data are used for Gibbs free energy minimization. For ternary compounds, conditions for a good fit between calculations and experiments might be more restrictive but the number of practical examples is not sufficient to derive a general law. In the special case of Ti_3SiC_2 deposited by CCVD, experimental and calculated results have been found in rather good agreement but some discrepancies have also been pointed out.^[9,10,16] According to the preceding reasoning, these discrepancies might be the consequence of some deviation from the “close to equilibrium conditions”.

In the present work more especially devoted to the formation of Ti_3SiC_2 by RCVD, thermodynamic calculations based on Gibbs free energy minimization have been worked out in the quinary system C-Cl-H-Si-Ti using the computer program Gemini 2 and data from the Scientific group Thermodata Europ, Saint Martin d’Hères, France. These data have already been used in references.^[12-14] In a first step, isothermal sections of the C-Si-Ti ternary subsystem were recalculated in full agreement with previous evaluations;^[17,18] Fig. 1 shows the section recalculated at 1100 °C. In a second step, solid-gas phase equilibria in the quinary system C-Cl-H-Si-Ti were considered. As the matter of concern was more especially the reaction between solid SiC and a gaseous mixture of H_2 and $TiCl_4$, as representation in the form of a triangle featuring SiC, H_2 , and $TiCl_4$ at the three apices with axis graduations in mole fraction, was chosen. Figure 2 shows the deposition diagram thus calculated at 1100 °C for a total gas pressure of 5 kPa. From this diagram, reaction between a $TiCl_4 + H_2$ gas mixture and solid SiC should yield pure Ti_3SiC_2 for hydrogen-rich gas mixtures ($H_2/TiCl_4$ molar ratios R higher than 3). For intermediate values of the molar ratio ($0.3 < R < 3$), TiC (either mixed with Ti_3SiC_2 or pure) should be produced in the gas-solid reaction. For gas mixtures very poor in hydrogen (molar ratio R lower than about 0.3), a part of SiC should be converted into TiC while the other part should be decomposed into elemental carbon. Excess silicon and carbon produced in the gas/solid reaction should be evacuated in the gas phase under the form of silicon chlorides $SiCl_2$ or $SiCl_3$ and methane CH_4 . This is

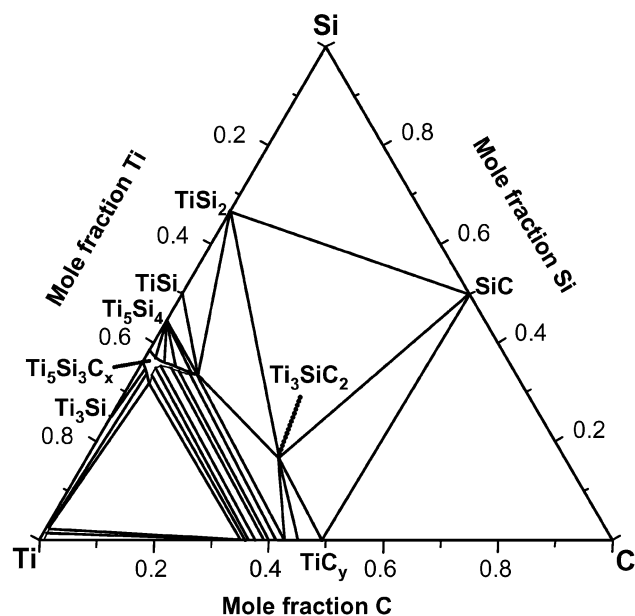


Fig. 1 Isothermal section of the C-Si-Ti phase diagram re-calculated at 1100 °C in full agreement with previous data^[17,18]

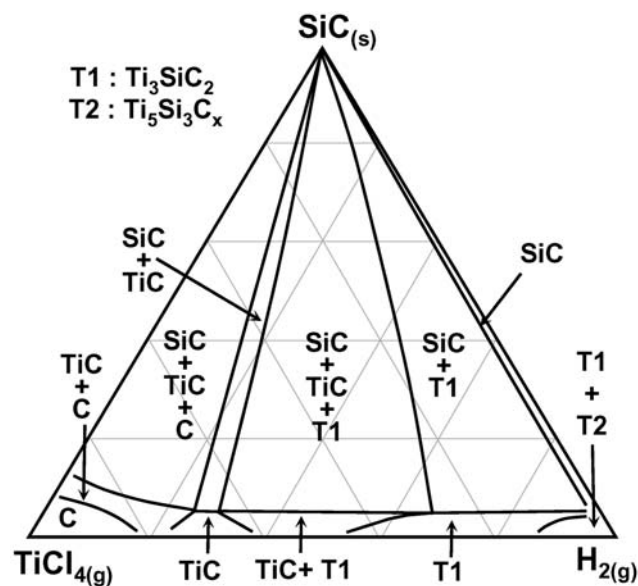


Fig. 2 Partial deposition diagram applicable to the formation at 1100 °C of RCVD coatings by reaction between solid SiC and a $H_2 + TiCl_4$ gaseous mixture at a total gas pressure of 5 kPa (phase fields very close to the border of the triangle are not represented)

indicated by the equilibrium compositions calculated for the reaction of 1 mol of SiC with a great excess of $TiCl_4 + H_2$ gaseous mixture under a pressure of 5 kPa. These compositions are: $x_{SiCl_2} = 0.48$ mol, $x_{SiCl_3} = 0.34$ mol, and $x_{CH_4} = 0.05$ mol at an R ratio of 0.5; $x_{SiCl_2} = 0.45$ mol, $x_{SiCl_3} = 0.34$ mol, and $x_{CH_4} = 0.036$ mol at an R ratio of 35.

3. Experimental Procedure

A classical low pressure hot wall CVD reactor equipped with a silica tube was used as in previous studies.^[13,14] Each RCVD layer was deposited on a polycrystalline graphite disk (12 mm in diameter, Ellor 30, Le Carbone Lorraine France) previously coated with a dense 0.5-3 μm thick film of 3C-cubic silicon carbide SiC. This film was deposited by CCVD at 1100 $^{\circ}\text{C}$ from a $\text{H}_2 + \text{CH}_3\text{SiCl}_3$ gaseous mixture at a pressure of 3 kPa (molar ratio $\text{H}_2/\text{CH}_3\text{SiCl}_3 = 4$). RCVD was then performed by reacting at 1100 $^{\circ}\text{C}$ the SiC film with a gaseous mixture of $\text{H}_2 + \text{TiCl}_4$ at a total pressure of 5 kPa, the molar ratio $R = \text{H}_2/\text{TiCl}_4$ varying from 4 to 35. Process Temperature Control Rings (LTH type from Ferro Electronic Materials B.V., Uden, The Netherlands) were used to determine the temperature within the deposition zone of the reaction tube. To facilitate characterization of the deposited layers and check the reproducibility of the RCVD process, several sequences consisting of an inner layer of CCVD-SiC and an outer layer of RCVD-coating were successively deposited on the same graphite discs.

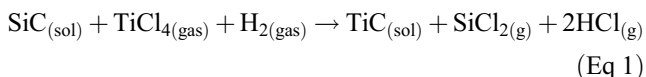
The RCVD layers thus produced were characterized by different techniques. X-ray powder diffraction (XRD, $\text{CuK}\alpha$ radiation) was performed on the reaction layers as-deposited on the graphite discs using a X'Pert Pro MPD diffractometer from Panalytical equipped with a back monochromator and a X'Celerator detector. The depth thus analysed by XRD was of the order of 10 μm . Observations were made by scanning electron microscopy on transverse fractures (SEM, Hitachi S-800 operated at 15 kV). Electron probe micro-analysis (EPMA, Cameca) was used to determine the chemical composition of the reaction layers. This was achieved on polished transverse sections at an accelerating voltage of 10 kV for a beam current of 9 nA. Atomic contents were determined by reference to pure element standards after correction for atomic number, absorption and fluorescence. Accuracy was of the order of ± 1 at.% for a lateral resolution of ± 0.7 μm .

4. Results

4.1 Thin RCVD Layers

Reaction layers with a thickness lower than 1 μm were grown at 1100 $^{\circ}\text{C}$ onto SiC at molar ratios $R = \text{H}_2/\text{TiCl}_4$ ranging from $R = 4$ to 35. According to the deposition diagram shown in Fig. 2, these experimental conditions should have been favorable to the formation of Ti_3SiC_2 .

In fact, the thin RCVD layers grown onto SiC at the molar ratio $R = 4$ only consisted of nearly stoichiometric titanium carbide TiC (cubic, $\text{Fm}\bar{3}\text{m}$, $a = 0.433$ nm). Not any indication for the formation of Ti_3SiC_2 was found. The corresponding chemical reaction can be schematically written:



A layer sequence $(\text{SiC}/\text{TiC})_n$ obtained by repeating deposition of SiC by CCVD for 8 min and subsequent

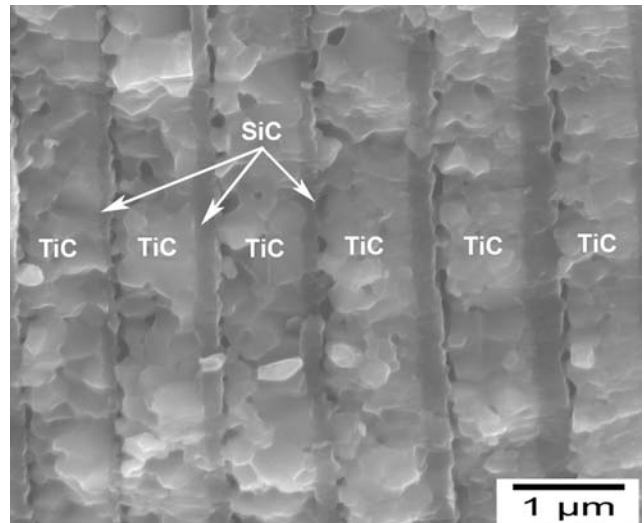
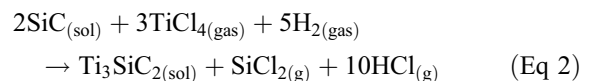


Fig. 3 Thin TiC layers grown in 20 min at 1100 $^{\circ}\text{C}$ onto SiC by RCVD from a $\text{TiCl}_4 + \text{H}_2$ gas mixture with a molar ratio $R = 4$ ($R = \text{H}_2/\text{TiCl}_4$)

partial conversion into TiC by RCVD for 20 min is shown in Fig. 3. It can be seen that the CCVD-SiC layers remains unconverted over a depth of about 200 nm. As to the layers of TiC grown by RCVD, they have a mean thickness of 800 nm and are made of round-shaped crystals with a diameter of the order of 200 nm. It should be noted that SiC is intimately bonded to each underlying TiC layer onto which it was deposited by CCVD: the interface is even and there is no lack of matter. Conversely, many voids are present at each interface between the TiC layer and the underlying SiC layer to the detriment of which TiC was grown.

To obtain RCVD thin layers containing the ternary carbide Ti_3SiC_2 instead of TiC, the molar ratio R had to be higher than 5. Figure 4 shows the periodic layer sequence grown at 1100 $^{\circ}\text{C}$ with the molar ratio $R = 35$. SiC was deposited in 3 min and then exposed for 10 min to the gaseous mixture $\text{TiCl}_4 + \text{H}_2$. Only two constituents were characterized by XRD in the resulting coating: Ti_3SiC_2 formed by RCVD and unconverted SiC (Fig. 5). The chemical solid-gas reaction can be schematically written:



As can be seen in Fig. 4, Ti_3SiC_2 forms continuous layers with a mean thickness of 1.3 μm . In these layers, the Ti_3SiC_2 crystals are bigger than the TiC crystals previously characterized and their shape is different. Indeed, the Ti_3SiC_2 crystals grown at $R = 35$ appear in the form of platelets with a mean size of 0.2×1.3 μm whereas the TiC crystals formed at $R = 4$ were globular with a diameter of 200 nm. The fact that most of these platelets are standing upright onto the incompletely converted SiC layers suggests a preferential orientation. Effectively, in the XRD patterns of such multi-layered coatings like that reported in Fig. 5, the

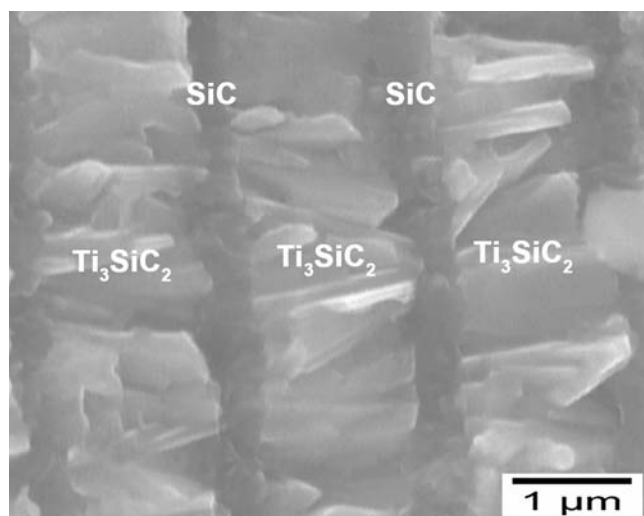


Fig. 4 Thin layers of Ti_3SiC_2 grown in 10 min onto SiC from a $\text{TiCl}_4 + \text{H}_2$ gas mixture with a molar ratio $R = 35$ ($R = \text{H}_2/\text{TiCl}_4$)

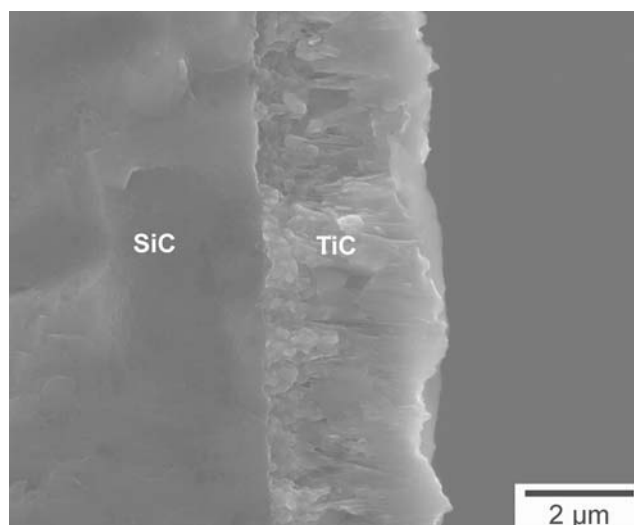


Fig. 6 Thick TiC layer produced by reacting SiC with $\text{TiCl}_4 + \text{H}_2$ ($R = 4$) under 5 kPa for 240 min at 1100 °C

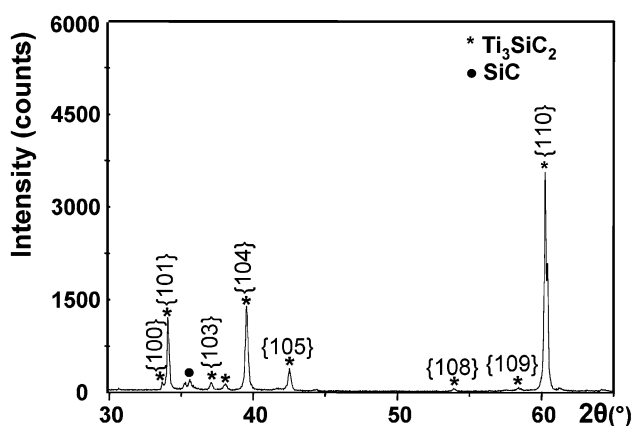


Fig. 5 XRD pattern ($\text{CuK}\alpha$ radiation) of a $(\text{SiC}/\text{Ti}_3\text{SiC}_2)_n$ multilayer coating. The fact that the (110) diffraction line characteristic for Ti_3SiC_2 is too strong while the (008) reflection is lacking indicates preferential orientation of the Ti_3SiC_2 platelets

(110) diffraction line characteristic for Ti_3SiC_2 is anomalously strong whereas the (008) reflection is lacking. This clearly confirms a preferential orientation of the c axis of the Ti_3SiC_2 crystals parallel to the SiC layer surface.

The foregoing results obtained for thin layers of TiC and Ti_3SiC_2 grown by RCVD onto SiC at 1100 °C are only in qualitative agreement with the deposition diagram shown in Fig. 2. Indeed, SiC is converted into Ti_3SiC_2 when the gas mixture is hydrogen-rich and into TiC when the gas mixture is hydrogen-poor as indicated by the deposition diagram. However, if the value of the R ratio is considered from a quantitative point of view, the experimental results do not fit well with the thermodynamic calculations. This misfit will be discussed later.

4.2 Thick RCVD Layers

In order to produce thick reaction layers, the reaction time corresponding to the deposition of SiC by CCVD and its conversion by RCVD was increased up to 240 min.

Figure 6 shows the reaction layer produced by heating SiC under a flowing gas mixture of $\text{TiCl}_4 + \text{H}_2$ for 240 min at 1100 °C at a molar ratio $R = 4$. As at shorter reaction times, titanium carbide TiC is the sole constituent of the 3 μm thick reaction layer thus obtained. This layer exhibits a duplex microstructure. In its inner part that extends over about 1 μm in thickness, the reaction layer consists of equiaxed round-shaped crystals with a mean diameter of 200 nm, like previously. In its outer part, the TiC crystals tend to be elongated in the growth direction giving to that part a more columnar appearance. These observations suggest that the inner part of the TiC reaction layer is the oldest and the outer the most recently deposited. An EPMA line profile was recorded point by point across the reaction layer from its inner part to its outer. A slight deviation from unity of the C/Ti molar ratio was thus revealed: the layer composition varied within the limits $\text{TiC}_{0.96}$ and $\text{TiC}_{0.82}$.

The increase in thickness of the TiC reaction layers grown at $R = 4$ has been plotted in Fig. 7 as a function of the deposition time. It can be seen that the rate of growth of TiC continuously decreases as the deposition time increases: initially of 30 nm min^{-1} , that rate becomes null for reaction times higher than or equal to 200 min. Such an important variation in deposition rate indicates that different processes successively control the growth of the reaction layer during the period of time investigated. More especially, three main stages can be distinguished:

1. As it is generally the case for most interface reactions,^[19] surface reactions should predominate in a former stage. In the present instance, unevenness has been noticed in Fig. 3 at the CCVD-SiC/RCVD-TiC interface. This suggests that the $\text{TiCl}_4 + \text{H}_2$ gas

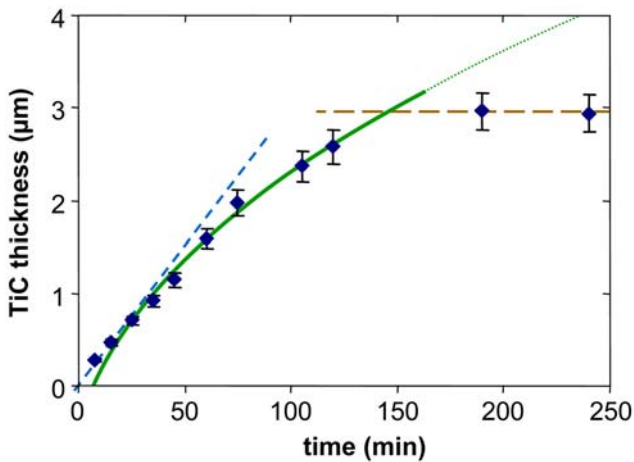


Fig. 7 Variation with the reaction time of the thickness of TiC layers produced onto SiC by RCVD from a $\text{TiCl}_4 + \text{H}_2$ gas mixture ($T = 1100\text{ }^\circ\text{C}$; total gas pressure: 5 kPa; $R = 4$)

mixture would attack the SiC surface in some places while in other places, this surface would be protected by TiC crystallites that nucleate and grow from the gas phase. When a gastight reaction layer is formed by stacking of TiC crystals (200 nm in diameter), surface reactions stop. The duration of this first stage controlled by surface reactions is less than 30 min under our experimental conditions.

- For reaction times ranging from 30 to 120 min, one enters a second stage in which evolution with time of the layer thickness, e , can be described by a branch of parabola having, when expressed under the reduced form $e^2 = Kt$, the following equation:

$$e^2 = 1.60 \times 10^{-15} t \quad (\text{Eq 3})$$

with t in second and e in meter ($0.6 < e < 2.5 \times 10^{-6}$ m). It is generally accepted that such a parabolic law characterize a growth process by solid-state diffusion of atoms.^[19,20] At the same temperature (1100 °C), a parabolic constant K of the same order of magnitude ($K = 2.9 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$) was reported for the diffusion-controlled growth of layers of small TiC crystals (100-200 nm in diameter) by reaction between a solid carbon substrate and a Sn-1wt.%Ti melt.^[21] Given that in the thick TiC reaction layers we have produced by RCVD, the carbide composition varies from $\text{TiC}_{0.96}$ to $\text{TiC}_{0.82}$, a Fick's coefficient of interdiffusion can be evaluated using the Fick's first law expressed as:

$$D_{\text{Fick interdif.}} = \left(\frac{K}{2}\right) \left(\frac{N_c}{\Delta N_c}\right) \quad (\text{Eq 4})$$

K being the parabolic growth constant in $\text{m}^2 \text{ s}^{-1}$ and $\Delta N_c/N_c$ the relative variation of the carbon molar fraction in the composition range $\text{TiC}_{0.98}$ - $\text{TiC}_{0.82}$. An interdiffusion coefficient of $9.4 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ has thus been obtained. On the other hand, an averaged Fick's coefficient of interdiffusion can be calculated at

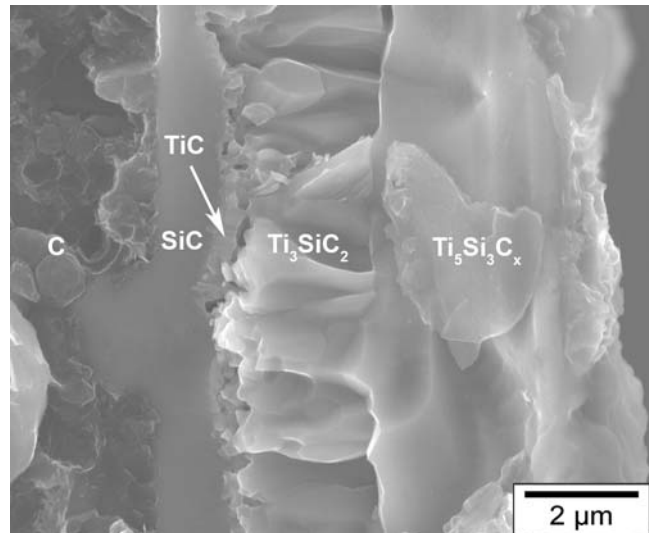


Fig. 8 Thick multi-component layer produced by reaction of $\text{TiCl}_4 + \text{H}_2$ with SiC at 1100 °C ($R = 4$; total gas pressure: 5 kPa; reaction time: 90 min)

1100 °C for the composition range $\text{TiC}_{0.96}$ to $\text{TiC}_{0.82}$ from the data by van Loo and Bastin^[22]. The value of this calculated coefficient is of $4.23 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$, i.e. about 200 times smaller than our experimental value. Very likely, the reason for that difference lies in the fact that grain boundary diffusion is predominant in TiC layers made of small crystals (200 nm) whereas van Loo and Bastin's data refer to volume diffusion in TiC layers consisting of very big grains (100 μm or more). On a comparison basis, a factor of 10^4 is reported for grain boundary versus volume diffusion in ZnO.^[23]

- For TiC reaction layers with a thickness larger than 2.5 μm , the growth rate more and more deviates from the parabolic law and finally, no growth at all occurs for reaction times longer than 200 min. Two additional processes can be invoked to explain why growth stops. One of these is the development of Kirkendall voids at the SiC/TiC interface. Effectively, carbon is virtually the only diffusing component in TiC_{1-y} , whatever the value of y ($0 < y < 0.5$).^[22] By reducing the contact area, such voids could slow down solid state diffusion. The other process is the evaporation of carbon at the solid gas interface under the form of gaseous CH_4 . This possibility is sustained by equilibrium calculations that give at $R = 0.5$ a non-negligible mole fraction of CH_4 ($x_{\text{CH}_4} = 0.05$) for 1 mol of SiC converted into TiC. Combination of diffusion controlled growth of TiC with evaporation of carbon can thus result under steady state conditions in a reaction layer that keeps a constant thickness, as demonstrated in reference.^[19]

Figure 8 shows the 6.5 μm thick reaction layer produced by RCVD after 90 min reaction at 1100 °C at a R ratio of 35. From XRD and EPMA characterization, this reaction layer consists of three different compounds arranged in three

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sublayers: a very thin sublayer of TiC in contact with unconverted SiC, a Ti_3SiC_2 intermediary sublayer only slightly thicker than after 10 min reaction (1.7 μm instead of 1.3 μm) and a $\text{Ti}_5\text{Si}_3\text{C}_x$ outer layer. The Ti_3SiC_2 intermediary layer exhibits the same columnar microstructure as that previously observed in thin layers, with a slight increase in crystals elongation. Exactly the same results were obtained for a thick RCVD layer grown on SiC in 30 min at 1100 °C at $R = 35$: simply, the total thickness was of 3.5 μm instead of 6.5 μm .

At this point it is interesting to compare the layers characterized after solid/gas RCVD at 1100 °C with reaction layers formed by interface reaction in SiC/Ti solid state diffusion couples. For such couples annealed at 1100 °C or less, the reaction zone mainly consists of a two-phased layer of TiC and $\text{Ti}_5\text{Si}_3\text{C}_x$,^[17,24-28] the presence of an additional Ti_3SiC_2 layer between SiC and the two-phased layer being sometimes mentioned.^[17,28] As a matter of fact, our results for thick layers formed at 1100 °C by RCVD are in relation with these data but do not match exactly. In this regard, it is worth noting that under our experimental conditions, the chemical activity of the titanium source is not equal to the unity but smaller. The driving forces for solid-state volume diffusion are also smaller, which reduces the rate of growth of the reaction layer and may slightly modify the layer sequence. More especially, phases that are mixed in the same layer at a high titanium activity (TiC and $\text{Ti}_5\text{Si}_3\text{C}_x$) may grow in two distinct layers at low titanium activity. This phenomenon has already been observed in solid state diffusion couples. For instance, the layer sequence SiC/ Ti_3SiC_2 /TiC + $\text{Ti}_5\text{Si}_3\text{C}_x$ /Ti characterized at 1100 °C in the presence of pure Ti was observed to turn to the sequence SiC/TiC/ Ti_3SiC_2 / $\text{Ti}_5\text{Si}_3\text{C}_x$ /Ti₃Al, the same reaction layer as in the present work, when pure Ti was replaced by the intermetallic compound Ti₃Al.^[28]

If the latter results obtained for thick layers grown at $R = 35$ are compared with the deposition diagram (Fig. 2), no fit at all can be found. Indeed, the thick reaction layers consist of three solid phases TiC, Ti_3SiC_2 , and $\text{Ti}_5\text{Si}_3\text{C}_x$ and there exists no phase field in the deposition diagram featuring these three compounds in equilibrium. Anyway, the three phases are arranged in three successive sub-layers and the gas phase or the SiC substrate are only in contact with one of these sub-layers. As a matter of fact, the deposition diagram is not valid to account for these results.

5. Discussion

In the following discussion, we will first try to provide a rational explanation for the points of agreement and discrepancy that have appeared between the calculated deposition diagram (Fig. 2) and the experimental results obtained by RCVD (Fig. 3-8). Then we will point out some principles for properly modelling the thermodynamic aspect of chemical reactions proceeding at the solid/gas interface in a multi-component system.

It has been recalled in Section 2 that “close to equilibrium conditions” at the solid/gas interface are needed for a

good fit between calculations and experiments in CCVD and that these conditions are generally fulfilled when reactions at the surface of the growing coating proceed at a fast rate compared with the rate at which the reactive species are supplied via the gas phase. Exactly the same requirements are needed in RCVD, but the situation is more complex since the substrate that is inert in CCVD plays an active part in RCVD. Consequently in CCVD all the elements that constitute the coating are coming from the flowing gas phase. Therefore, the rate at which all species are brought to the growing coating remains constant under steady state conditions and if close to equilibrium conditions are established at the beginning of the deposition process, they will no more change. Conversely in RCVD at least one reactive species is coming from the substrate. The deposition rate may thus continuously decrease as the substrate is partly and then completely covered by a reaction layer of increasing thickness.

From there, two different stages have to be distinguished in a RCVD process:

1. first stage during which the RCVD coating is discontinuous or porous, which allows a direct contact to be established between the gas phase and the solid substrate;
2. second stage where a dense and continuous reaction layer has formed at the substrate surface isolating it from the gas phase.

The important change in deposition rate observed in our experiments between thin and thick layers produced at $R = 4$ as well as at $R = 35$ corresponds to the transition from the first stage to the second one.

During the first stage of the RCVD process, i.e. during the fast rate growth of thin layers of TiC or Ti_3SiC_2 , experimental results are qualitatively in agreement with the deposition diagram. By analogy with CCVD, one can consider that “close to equilibrium” requirements are grossly met at the solid/gas interface or, in other words, that the surface reaction processes involved in the consumption of SiC and formation of TiC or Ti_3SiC_2 crystals develop at a sufficiently fast rate compared with gas phase transport or diffusion. Quantitatively, however, there is a shift between calculated and observed results with respect to the H_2/TiCl_4 molar ratio R . In part, it can be considered that the real value of the R ratio in the hot deposition zone near the SiC substrate surface is smaller than that fixed in the gas mixture entering into the reactor: several technical reasons have been given to account for that assumption.^[14] It can also be thought that another part of the shift traduces some “supplementary” deviation to the close to equilibrium conditions that should be specific to the formation of the ternary compound Ti_3SiC_2 , as previously evoked in Section 2.

Figure 9 shows the variations of the chemical potentials of C, Si, and Ti in the vicinity of the solid/gas interface in the case of thin RCVD coatings. Activity values for solid phases were taken from reference.^[29] Meeting the “close to equilibrium requirements” implies that the chemical potentials of the constituting elements monotonously vary

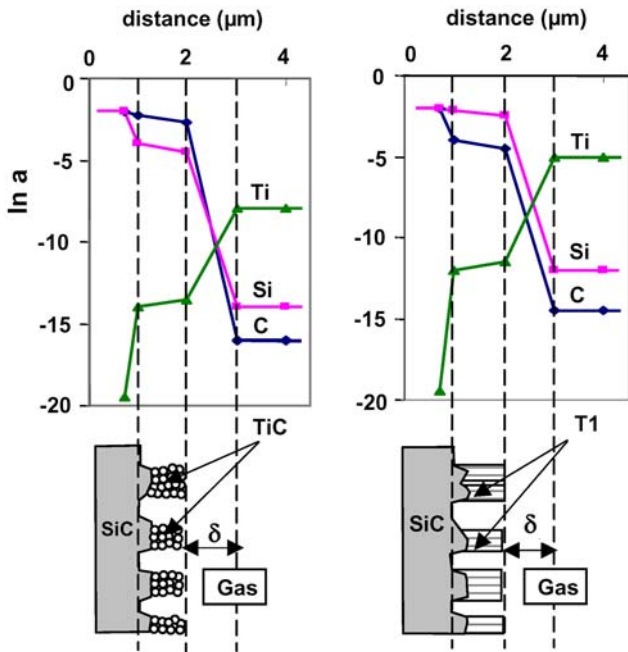


Fig. 9 Variation of the chemical activities of C, Si, and Ti at the crossing of thin RCVD layers grown at 1100 °C onto SiC at $R = 4$ (TiC on the left) and $R = 35$ ($T_1 = \text{Ti}_3\text{SiC}_2$ on the right)

without discontinuity at the crossing of the different interfaces (only the compositions change abruptly). As long as a three-phased equilibrium tends to be established between the gas phase, the growing coating and the SiC substrate, the degrees of freedom for the system are limited and chemical potentials vary only slightly in the deposition zone. In that first stage where gas phase diffusion is rate limiting, most of the variations in chemical potential occur in the boundary layer, δ , as shown in Fig. 9.

Once a continuous and dense reaction layer is formed at the substrate surface by RCVD, this layer naturally acts as a (permeable) diffusion barrier. From that moment, further reaction between the substrate and the gas phase can only proceed by solid-state diffusion of atoms through the barrier layer. Solid-state diffusion being much slower than gas phase diffusion, the former process will rapidly become rate limiting. Under kinetic control by solid-state diffusion, there is no more need for a three-phase equilibrium to be established between the gas phase, the growing coating, and the substrate. Only two-phased solid-solid or solid-gas equilibria are required at the different interfaces. This increases the degrees of freedom for the system and while the chemical activity gradients of the constituents will tend to disappear in the boundary layer, δ , they will develop in the barrier layer, as shown in Fig. 10. As a general rule for interface reaction layers growing by diffusion, intrinsic diffusion of one type of atoms can only proceed down its activity gradient.^[20] It is clear from Fig. 10 that carbon and silicon can diffuse outwards while titanium diffuses inwards. For these thick RCVD layer configurations the gas phase is no longer in contact with the substrate and for that reason, the deposition diagram is no longer valid.

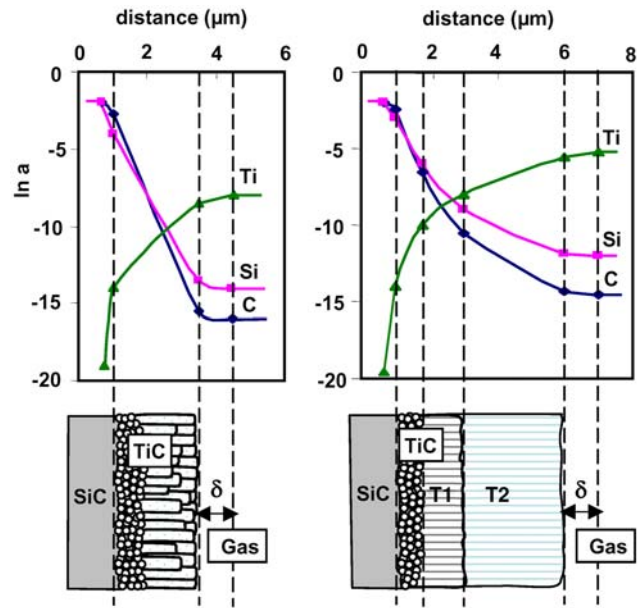


Fig. 10 Chemical activities of C, Si, and Ti at the crossing of thick RCVD layers grown at 1100 °C onto SiC at $R = 4$ (on the left) and $R = 35$ ($T_1 = \text{Ti}_3\text{SiC}_2$, $T_2 = \text{Ti}_5\text{Si}_3\text{C}_x$ on the right)

To sum up, modelling the evolution of thick RCVD reaction layers terminates in description of the growth of reaction layers by solid-state diffusion in an open system. Qualitatively, the diffusion path concept may be useful to understand the development of complex reaction zones.^[20,30] Assuming that local phase equilibria exist at the different interfaces under steady state growth conditions, intrinsic diffusion of atoms proceeds down their chemical potential gradient, as shown in Fig. 10. For a quantitative description of the growth of thick reaction layers by RCVD, the solid-state reaction-diffusion models based on Fick's law^[20,29-33] or on the Nernst-Einstein formalism^[34] should be the most appropriate.

6. Conclusions

A deposition diagram has been calculated at 1100 °C by Gibbs free energy minimization in the C-Cl-H-Si-Ti quinary system in order to produce Ti_3SiC_2 layers by RCVD onto a SiC substrate. In qualitative agreement with that diagram, thin layers of pure Ti_3SiC_2 (up to 1.3 μm thick) were produced in 10 min onto SiC by reactive CVD from a $\text{TiCl}_4 + \text{H}_2$ mixture (total gas pressure: 5 kPa; molar ratio $\text{H}_2/\text{TiCl}_4 = 35$). Under the same experimental conditions but for longer reaction times (30 min or more), the reaction layers were thicker and two sublayers were observed to develop at each side of the Ti_3SiC_2 first formed layer: an inner TiC sublayer and an outer $\text{Ti}_5\text{Si}_3\text{C}_x$ one. As a matter of fact, the calculated deposition diagram was no more appropriate to account for the growth of these thick multiphased layers. Valuable qualitative description of a

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RCVD process in the case of thick, continuous and multiphased layers has to be based on the diffusion path concept and chemical activity considerations. As to quantitative modelling, it needs use of diffusion-reaction models specially developed for solid-state diffusion couples.

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