



Transient stages during the chemical vapour deposition of silicon carbide from $\text{CH}_3\text{SiCl}_3/\text{H}_2$: impact on the physicochemical and interfacial properties of the coatings

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ABSTRACT

Transient chemical vapour deposition experiments were produced from MTS/ H_2 mixtures by varying the deposition temperature or the gas flow rates (Q_{MTS} or Q_{H_2}) versus time. The gas phase, deposition rates and properties of the transient coating (φ_{Tr}) were investigated and adhesion assessments of $\text{SiC}/\varphi_{\text{Tr}}/\text{SiC}$ bilayers were performed by scratch testing. Transient stages resulting from a decrease of Q_{MTS} or temperature lead to silicon co-deposition, but do not affect interfacial properties. Transient stages resulting from a decrease of Q_{H_2} eventually lead to carbon co-deposition. Thick and continuous carbon interlayers lead to a poor adhesion whereas thin and discontinuous layers do not.

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1. Introduction

The need of refractory materials for use in particularly harsh conditions has led to significant advances in many fields of the materials science [1]. These high temperature components are usually coated to protect them against corrosion, intense heat fluxes or wear. Silicon carbide (SiC) is a coating material of choice because of its exceptional properties (chemical inertness, thermal conductivity, hardness...). SiC coatings are employed for instance to protect chemical reactors, space mirrors, thermostructural composite materials or the fission fuel containers of the future nuclear reactors. Chemical vapour deposition (CVD) is the most often used technique to deposit SiC coatings, because it allows an excellent control of their composition, structure and thickness uniformity. An important precaution during the synthesis of CVD coatings is the control of the adherence of the coating to the substrate or between different layers, in a multilayer coating.

When a SiC coating is synthesised by CVD, the experimental parameters (temperature, pressure, gas flow rates) vary significantly before and after steady state deposition, at the beginning and at the end of the process. The conditions may also be altered accidentally in a variable extent during a steady phase of deposition. These CVD

transient stages may result in the deposition of superficial or confined layers having singular chemical and structural properties. When a transient stage occurs, for instance, during the starting up of the process, before the regular deposition stage, or between two steady phases, an interfacial layer is formed that can sometimes lead to the debonding of the outer SiC layer [2]. The objective of the present work is to reproduce, in a controlled manner, different types of transient stages, and to examine their consequences on the adhesion between two SiC layers. By analogy with ceramic matrix composites (CMC), where this term refers to the intermediate layer(s) between a fibre and the matrix [3], we will use interphase or transient interphases (φ_{Tr}) to define an interfacial layer resulting from a transient deposition stage which is covered with a SiC outer layer. Yet, the context of this work is not to develop new interphases, aiming at the proper deviation of cracks, as in CMC [3], but rather to understand the formation of transient interphases in certain CVD conditions and eventually the reason why they can cause the debonding of the outer coating.

Methyltrichlorosilane (CH_3SiCl_3 , MTS) diluted in hydrogen (H_2) is the most commonly used single-source SiC precursor, mainly because of its composition ($\text{Si}/C_{\text{at}} = 1$), vapour pressure, thermal stability, but also for the high properties of the resulting coatings. A considerable amount of work has been conducted on the CVD from MTS/ H_2 mixtures for more than 40 years [2,4–51]. It rapidly appeared from these studies that the homogeneous chemistry resulting from the thermal decomposition of MTS is particularly complex and plays a critical part in the deposition process [6–12]. From the early times

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to very recently, theoretical-thermodynamic and kinetic- approaches have been proposed to describe the homogeneous reactions taking place in the reactor and the nature of the gas species, particularly of the effective precursors of the Si–C solid [13–23]. In parallel, experimental studies have been conducted to investigate the influence of the CVD parameters on the growth rate [25–36,38–48,50–51], the composition of the gas phase (in situ or downstream of the reactor) [6–12,50], the nature (i.e. the stoichiometry and the structure) of the deposited solid [10,11,29,32,34,36,37,39–43,47–51] and even its mechanical properties [24,25]. Several authors have even combined these various aspects to develop models to predict the growth rates [34,38,39,45,47]. Some experimental results however, even when obtained at comparable deposition temperature, are sometimes scattered because of the very wide range of residence time (t_r) of the reactive gas mixture in the deposition chamber. This parameter, which controls the homogeneous reactions, is indeed strongly related to the various conditions of total pressure (reduced or atmospheric), gas flow and reactor geometry explored in these studies.

The present report considers only isothermal and low pressure-isobaric CVD, because these conditions are more suited to the industrial production of SiC-based coatings or composites, of large size and at large scale [52,53]. Even within these restricted conditions, the CVD from the MTS/H₂ system at constant T and P, and given initial gas phase composition (usually defined by the standard gas flow ratio $\alpha = Q_{H_2}/Q_{MTS}$), has been extensively studied [27,28,30–36,39,41–44]. The correlation between thermodynamic calculations, the monitoring of the gas species formed in the reactor, the growth kinetics and the characterization of the solid, has allowed proposing homogeneous and heterogeneous (adsorption, nucleation and growth) reaction mechanisms [32,33,39].

If the present study can definitely rely on these previous works, the conditions of initial gas precursor composition and temperature encountered during typical transient stages can notably deviate from those already explored. It has been therefore necessary to complete these studies by investigating a more extended range of steady conditions and, particularly, of parameter α .

After this preliminary work on steady stage but non-conventional CVD conditions, the second part of the study is dedicated, properly speaking, to transient state CVD. Three types of transient stages have been considered, which consist in decreasing either: (i) the temperature, or (ii) the MTS flow rate, or (iii) the H₂ flow rate. The consequences on the composition of the gas phase and the deposition kinetics have been respectively examined by in situ FTIR and thermogravimetric analyses. The chemical and structural properties

of the resulting transient coatings have been analysed in detail and correlated with the previous investigations on the homogeneous reactions and the deposition rates.

Finally, the adhesion of various SiC/ φ_{Tr} /SiC bilayers (two adjacent SiC layers separated by a certain type of transient interphase φ_{Tr}), has been assessed using scratch testing. The results have been discussed on the basis of the CVD conditions and the chemical and structural properties of the interphase.

2. Experimental procedures

The CVD apparatus is shown in Fig. 1. It is a vertical hot wall reactor operating at reduced pressure. It consists of a silica tube (100 mm in inner diameter), heated in its central part by radio-frequency. The quasi-isothermal deposition zone ($\pm 5^\circ\text{C}$) is approximately 100 mm-long. The coatings were deposited on small pellets of single crystal silicon wafer ($20 \times 10 \times 0.5 \text{ mm}^3$), previously cleaned in ethanol and heated under a pure H₂ flow before starting deposition.

All the coatings were prepared in conditions deviating more or less from the reference condition defined by: a total pressure $P = 5 \text{ kPa}$, a temperature $T = 1000^\circ\text{C}$, a precursor gas ratio $\alpha = 3$ and a total gas flow rate $Q_{tot} = 200 \text{ sccm}$. The whole range of conditions explored was: $P = 5$ or 10 kPa , $T = 750\text{--}1050^\circ\text{C}$, $\alpha = 0\text{--}\infty$, $Q_{tot} = 100\text{--}400 \text{ sccm}$.

A high sensitivity microbalance (BSetsys from Setaram) was connected to the top of the reactor, specifically for the in situ measurements of the deposition kinetics. The specimen was hung to the balance, allowing the acquisition of the deposition rate (in $\text{mg min}^{-1} \text{ cm}^{-2}$) at a given position in the hot zone of the reactor.

A Fourier-transform infrared (FTIR) spectrometer (Nicolet 550, run with OMNIC) was coupled to the CVD reactor [54]. The in situ detection of the reactants, intermediates and product species and a semi-quantitative analysis of the gas concentrations (peak areas) were performed in the transmission mode (the incident IR beam going axially through the reactor before reaching the HgCdTe detector).

The uniformity and the average chemical composition of the coatings (with an error of approximately $\pm 2 \text{ at.}\%$) were characterised by recording in-depth Auger electron spectroscopy (AES) concentration profiles (VG Microlab 310-F). The accelerating voltage and the beam current were respectively 10 kV and 5 nA. The Si and C concentrations were obtained using sensitivity factors inferred from the analysis of a SiC standard. The etch depth was calibrated using standard Ta₂O₅ layers.

The morphology of the free surface and fractured cross-sections of the coatings was observed by field emission gun scanning electron

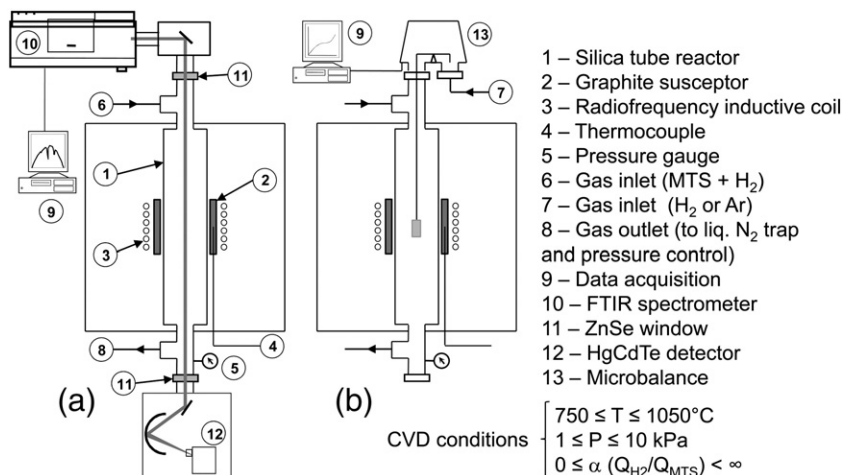


Fig. 1. CVD reactor geometry and configuration during (a) in situ gas phase analysis and (b) measurement of the deposition rate.

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