



Reactive chemical vapor deposition of Ti_3SiC_2 with and without pressure pulses: Effect on the ternary carbide texture

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ABSTRACT

Ti_3SiC_2 layers were grown by reactive chemical vapor deposition (RCVD) of a H_2/TiCl_4 gaseous mixture on previously deposited SiC layers. A comparison was made between classical RCVD in which the gases continuously flow at a constant low pressure during several minutes in the reactor and pressure-pulsed RCVD (P-RCVD) in which the reactor is (re)filled with the H_2/TiCl_4 gas and (re)emptied every few seconds. Long duration single treatments resulted in similar thick multi-phased coatings growing by solid state diffusion with both RCVD and P-RCVD methods. Conversely, in relation with the steps of nucleation and growth by surface reaction, the repetition of short duration SiC deposition/RCVD sequences with or without pressure pulses gave rise to Ti_3SiC_2 coatings with different textures.

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1. Introduction

Thanks to its unique properties [1], the Ti_3SiC_2 MAX phase has interesting potential applications in prospect as thin layers: interphases in ceramic matrix composites (CMCs) [2], electrical [3,4] and tribological [5] contact layers at high temperature, lead–bismuth corrosion-resistant materials [6] or fuel coatings [7] in nuclear reactors. This lamellar material with a hexagonal structure in which the basal planes (001) are weakly bonded exhibits anisotropic mechanical and electrical properties [8,9]. Ti_3SiC_2 films can be produced by physical vapor deposition [10] and by conventional chemical vapor deposition (CVD) from gas mixtures containing the three elements Ti, Si and C [11–15]. Unlike with the physical method, with the conventional CVD method Ti_3SiC_2 is systematically deposited with the weakly bonded basal planes preferentially oriented perpendicular to the substrate surface. This feature can be detrimental to some aimed applications such as crack deflection from mode I to mode II in CMC interphases or diffusion barriers.

An alternative method for obtaining Ti_3SiC_2 deposits consists in using reactive CVD (RCVD) instead of conventional CVD. In this method a Ti_3SiC_2 layer grows by reaction of a H_2/TiCl_4 gaseous mixture with a previously deposited SiC coating used as solid carbon and silicon sources. In a previous study, the RCVD method was combined with a pressure-pulsed CVD method (P-RCVD) but the ternary phase could not

be obtained pure; most often, it was mixed with TiC [16]. A first problem was the impossibility to exceed several nanometers in thickness for the SiC layer first grown by RCVD from SiCl_4 and pyrocarbon because carbon hardly diffuses through stoichiometric SiC. Another difficulty was the value of the dilution ratio of TiCl_4 in H_2 (R) that was chosen too low. Indeed, in further studies in which the use of pressure pulses was renounced, it was established that the growth of thin continuous layers of pure Ti_3SiC_2 by “classical” low pressure RCVD is feasible if and only if R is high enough; otherwise, TiC is obtained [17,18].

The aim of the present paper was to remedy the difficulties encountered in the earlier work, i.e. to convert SiC continuous layers into Ti_3SiC_2 by P-RCVD thanks to a high enough dilution ratio R , and to study the influence of the pressure pulses on the coating texture by comparison with the classical RCVD method.

2. Experimental procedure

2.1. Deposition procedure

The processing procedure has been previously described for the classical case (RCVD without pressure pulses) in reference [17] and for the pressure-pulsed method (P-RCVD), though modified, in reference [16]. Briefly, in both cases (classical RCVD and P-RCVD) the same apparatus was used; the coatings were deposited at 1100 °C on polycrystalline graphite disks placed inside the hot area of the horizontal hot-wall CVD reactor chamber. In each case, a SiC sub-layer was previously deposited from H_2 and CH_3SiCl_3 (MTS) with a ratio $[\text{H}_2]/[\text{MTS}]$ equal to 4. Then, after

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vacuum gas removal, the $\{H_2/TiCl_4\}$ gaseous mixture was introduced in the reactor, which allowed the growth of Ti_3SiC_2 layer(s) by SiC consumption. The titanium tetrachloride vapor was carried by hydrogen through a bubbler and a tank at room temperature. The reactant concentration ratio R ($[H_2]/[TiCl_4]$) was adjusted as high as 35 by adding pure H_2 with an extra parallel hydrogen feed line.

The differences between both methods are detailed as follows:

- In the classical case, the total pressure was maintained in the reactor at a constant value during the deposition of each kind of layer by a vacuum pump through a regulating valve and a pressure gauge. The pressure was 3 kPa for SiC deposition by CVD and 5 kPa for Ti_3SiC_2 growth by RCVD. During each sub-layer growth, the gases flowed continuously at a constant rate in the open reactor from the entrance to the outlet. In a run, the deposition sequence (CVD treatment at 3 kPa with $\{H_2/MTS\}$, vacuum gas removal, RCVD at 5 kPa with $\{H_2/TiCl_4\}$, and vacuum gas removal) could be repeated several times (n) in order to obtain a coating thick enough for further characterization. A repetitive deposition sequence was designated as $(S_{s'}/T_{t'})_n$ where s' was the number of minutes used for each previously SiC sub-layer deposition, t' the time in minutes chosen for each Ti_3SiC_2 sub-layer growth and n the total number of repeated sequences. The minimum values for s' and t' were of 3 min. Fig. 1a shows the variation of pressure in the reactor versus time during a $(S_3/T_3)_1$ bi-layer processing.
- In the second case, the regulating valve was removed and pressure pulses were obtained within the chamber by opening and closing pneumatic valves at regular intervals through an automatic controller. A pulse consists in the brief introduction of the gas mixture into the reactor chamber, the reaction in the closed chamber for 5 s and the gas evacuation through the vacuum pump during 5 s. The maximum pressure of a pulse

was determined by the supply pressure monitored in the upstream tankers. The supply pressure of the gaseous mixture was 10 kPa both for SiC deposition by P-CVD from $\{H_2/MTS\}$ and for Ti_3SiC_2 growth by P-RCVD from $\{H_2/TiCl_4\}$. The coatings were named $(S_{(s)},T_{(t)})_n$ where s was the number of gas pulses chosen for each SiC sub-layer deposition and t was the number of $TiCl_4/H_2$ pulses used for Ti_3SiC_2 deposition. The example of a pressure cycling given in Fig. 1b corresponds to the deposition of one $(S_{(3)},T_{(2)})_1$ bi-layer.

2.2. Characterization

The coated disk surfaces were characterized by X-ray diffraction (XRD: X'Pert Pro MPD from Panalytical, equipped with an X'Celerator detector and a diffraction beam monochromator, $CuK\alpha$ radiation, Almelo, The Netherlands). Then, coated graphite disks were broken and the fracture surfaces of the coatings were observed with a scanning electron microscope (SEM: S800 from Hitachi, Tokyo, Japan) operating at 15 kV. With thick enough sub-layers (i.e. above 1 μm), cross section compositions were determined by electron probe micro-analysis (EPMA: CAMEBAX from CAMECA, France) as previously described [17,18].

3. Results and discussion

3.1. Thick coatings produced by single duration RCVD and P-RCVD treatments

First, single long duration treatments were performed using both classical RCVD and P-RCVD methods, the deposition sequences being $(S_{60}/T_{90})_1$ and $(S_{(500)}/T_{(720)})_1$, respectively. EPMA, SEM (Fig. 2) and XRD (Fig. 3) show that except for the layer thickness which is greater in classical RCVD than in P-RCVD (effective deposition times are not the same), very similar results are obtained. For both coating methods, a part of the volume of first deposited SiC layer remains unconverted. Its surface is covered with three sub-layers: an inner sub-micrometric TiC layer, a Ti_3SiC_2 layer exhibiting a plate-like microstructure and an outer $Ti_5Si_3C_x$ layer. In the case of classical low pressure RCVD, the Ti_3SiC_2 sub-layer is clearly textured with plates orientated perpendicular to the substrate surface (Fig. 2a). Although it is difficult to confirm this feature by XRD because of the presence of $Ti_5Si_3C_x$ reflections, the preferential orientation of Ti_3SiC_2 plates seems less pronounced in the case of P-RCVD (Fig. 2b).

Previous work has shown that the growth of thick three-phased coatings by classical RCVD is controlled by the solid state interdiffusion of carbon, silicon and titanium atoms through the whole three-phased coating. In this growth process, each of the three elements intrinsically diffuses down its chemical potential gradient, in accordance with the diffusion path concept [18]. On the basis of the great similarities in nature, morphology and composition between the two thick three-phased deposits, it can be assumed that growth of thick coatings either by classical RCVD or P-RCVD is controlled by the same solid state volume diffusion mechanism. Concerning more especially the Ti_3SiC_2 sub-layer, presence of TiC at its inner side and of $Ti_5Si_3C_x$ at its outer side brings evidence that the three elements C, Si and Ti effectively diffuse through it.

Other single duration treatments, i.e. $(S_{s'}/T_{t'})_1$ and $(S_{(s)},T_{(t)})_1$, were performed at the same temperature, 1100 °C, for shorter deposition times. This allowed the spatiotemporal growth diagrams presented in Fig. 4 to be drawn.

In broad outline, the diagrams drawn for classical RCVD and P-RCVD are very similar. For both coating methods, a layer of pure Ti_3SiC_2 is first formed onto SiC. When the thickness of this first layer attains a critical value, e_{crit} , another layer of $Ti_5Si_3C_x$ develops onto it. At last, a TiC layer with globular fine grains (50–100 nm) appears and slowly grows between Ti_3SiC_2 and SiC. It can moreover be seen in Fig. 4 that growth of all the thick multi-phased layers ($e > e_{crit}$) produced by classical RCVD or

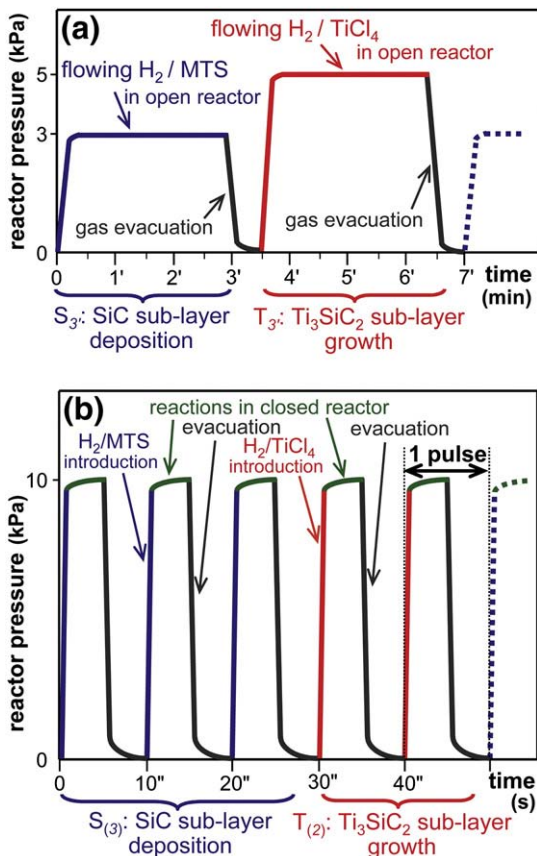


Fig. 1. Examples of a gas sequence $(S_3,T_3)_1$ in classical (R)CVD (a) and of a pressure-pulsed gas sequence $(S_{(3)},T_{(2)})_1$ in P-(R)CVD (b) for the processing of bi-layers.

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