Kinetic laws of the chemical process in the CVD of SiC ceramics from $\text{CH}_3\text{SiCl}_3\text{-H}_2$ precursor

F. LOUMAGNE, F. LANGLAIS and R. NASLAIN

*Laboratoire des Composites Thermostructuraux, UMR 47, CNRS-SEP-UB1, Domaine Universitaire,
3 Allée de la Boétie, 33600 Pessac, France*

ABSTRACT - On the basis of growth rate measurements as a function of temperature and initial gas phase composition, the kinetic process of the CVD of silicon carbide from MTS-H_2 is investigated, particularly under conditions of rate-control by the chemical reactions. Within specific ranges of dilution ratio $3 \leq \alpha \leq 5$ and total pressure $5 \leq P \leq 10 \text{ kPa}$, two kinetic regimes are brought out depending on the temperature. At about 825°C , the deposition of SiC could be rate-limited by the homogeneous decomposition of MTS with an activation energy higher than 300 kJ.mol^{-1} and an apparent reaction order of 2.5 with respect to MTS. At about 925°C , surface reactions could control the overall kinetic process with an activation energy of only 160 kJ.mol^{-1} and an inhibitor chemisorption of Cl species which involves a negative reaction order with respect to HCl.

1- INTRODUCTION

Silicon carbide prepared by chemical vapour deposition (CVD) can be integrated in advanced electronic devices and ceramic matrix composites if specific conditions of relatively low temperature and low pressure are used [1]. Among the various possible precursors in both chemical systems Si-C-H and Si-C-H-Cl, the CH_3SiCl_3 (MTS)/ H_2 gaseous mixture was very often chosen [2-5].

Under these T-P conditions, the kinetic laws which govern the chemical processes involved in the CVD of SiC are needed, with a view to understand the deposition mechanisms and to model both the infiltration of porous substrates (CVI) [6, 7] and the various phenomena occurring in the CVD/CVI reactors. These kinetic data can only be acquired experimentally and up to now, very little is known in this field. Kinetic studies have been carried out under atmospheric pressure and have resulted in (i) activation energies within a large range of values ($70 - 400 \text{ kJ.mol}^{-1}$), depending on the deposition temperature [8, 9] and (ii) a first order with respect to MTS [9]. Under reduced pressure ($P=3.3 \text{ kPa}$), a temperature of about 1000°C and a ratio $\alpha = P_{\text{H}_2}/P_{\text{MTS}}$ between 5 and 20, Besmann and Johnson have determined an activation energy of 188 kJ.mol^{-1} and a zero-order with respect to MTS [10]. The inhibition of the SiC deposition by the HCl by-product was also evidenced by Besmann et al. for $P=100 \text{ kPa}$, $T=1100^\circ\text{C}$ and $10 < \alpha < 20$ [11]. On the other hand, according to thermodynamic calculations, the deposition of silicon carbide was assumed to result from two successive chemical steps : (1) a homogeneous decomposition of MTS in hydrogen giving rise to intermediate reactive species and (2) a heterogeneous reaction between these actual gaseous precursors [12]. A kinetic

investigation of the first step, carried out under atmospheric pressure and low temperatures, revealed a high activation energy of 336 kJ.mol^{-1} , a first-order with respect to MTS and a zero-order with respect to hydrogen [13]. At last, very recently, a study of the growth rate in the MTS/ H_2 system as a function of total gas flowrate, temperature and total pressure, has permitted to define accurately the conditions for a kinetic process controlled by the chemical reactions [14].

The purpose of the present contribution is to investigate the influence of (i) the temperature and (ii) the composition of the gas phase on the deposition rate for $1 \leq \alpha \leq 5$; $3.5 \leq P \leq 10 \text{ kPa}$ and two temperatures (i.e. 825 and 925°C) corresponding to different activation energies. On the basis of a chemical analysis of the deposits, conditions for pure SiC deposition have been defined and overall kinetic laws proposed.

2- EXPERIMENTAL

The deposition experiments have been carried out on graphite substrates in a cylindrical hot-wall low pressure vertical reactor heated by radio-frequency induction (fig. 1) with a large hot isothermal zone and a creeping laminar flow. The growth rate measurements were performed in-situ with a microbalance (sensitivity of $2.5 \mu\text{g}$). The influence of the partial pressures of MTS and H_2 was studied by varying α ratio (one partial pressure is varied and the other is constant) and pressure P . For HCl and CH_4 influence, additional amounts of these species were introduced in the initial gaseous mixture. The deposits have been characterized by X-ray diffraction and some of them analysed by electron probe X-ray microanalysis (EPMA) and electron energy loss spectroscopy (EELS)

Figure 1 : Schematics of the CVD equipment

3- GROWTH KINETICS

3.1- Influence of temperature

The growth rate is plotted in figure 2 as a function of the reciprocal temperature for $Q=200\text{sccm}$, $\alpha=3$, $P=1$ and 10kPa . Three domains are evidenced in these plots :

(i) For all conditions, at low temperatures ($T < 850 - 900^\circ\text{C}$), the deposition is highly thermally activated. The activation energy is higher than 300 kJ.mol^{-1} , which means that the kinetics is governed by chemical reactions.

(ii) For $T > 900^\circ\text{C}$, $\alpha=3$ and $P=1\text{kPa}$ and for $850 < T < 950^\circ\text{C}$, $\alpha=3$ and $P=10\text{kPa}$, the deposition kinetics is controlled by chemical reactions, but with a lower activation energy, i.e. $160 \pm 40\text{ kJ.mol}^{-1}$.

(iii) At high temperatures ($T > 950^\circ\text{C}$ for $\alpha=3$ and $P=10\text{kPa}$), the deposition process is not thermally activated. Mass transfers control the kinetics.

A temperature within each domain corresponding to thermally activated processes is chosen for the study of the influence of the gas phase initial composition on the growth rate, i. e. 825 and 925°C .

Figure 2 : Growth rate variations with reciprocal temperature for $Q=200\text{sccm}$

3.2- Influence of MTS partial pressure

The variations of the growth rate with MTS partial pressure are reported in a log-log scale in figure 3 for $P_{\text{H}_2}=4.2\text{kPa}$ and for both temperatures 825 and 925°C . In these experiments, as P_{MTS} increases from 0.8 to 4.2 kPa , the total pressure is raised from 5 to 8.3 kPa , α ratio decreases from 5 to 1 and the total flow rate increases from 200 to 330 sccm ($\text{standard.cm}^3.\text{min}^{-1}$).

When the deposition kinetics is highly thermally activated ($T=825^\circ\text{C}$), a drastic influence of MTS content is observed. The growth rate is greatly favoured by an increase of MTS partial pressure on low P_{MTS} values side (the corresponding apparent reaction order is 2.5) and highly inhibited on the high P_{MTS} values side (with an apparent reaction order of -3). A large maximum is observed between these behaviours corresponding to an apparent zero order in MTS.

For $T=925^{\circ}\text{C}$, the growth rate is higher and its variations with P_{MTS} exhibit a similar behaviour, which is however less pronounced. For low MTS partial pressures, the growth rate is almost constant (with $n \approx 0.1$), and for $P_{\text{MTS}} > 2.5 \text{ kPa}$, a reaction order of -1 is derived.

Figure 3 : Growth rate variations with MTS partial pressure for $P_{\text{H}_2}=4.2 \text{ kPa}$ and $Q_{\text{tot.}}=200\text{-}330 \text{ sccm}$

3.3- Influence of H_2 partial pressure

The growth rate is plotted in figure 4 as a function of H_2 partial pressure for $P_{\text{MTS}}=1.7 \text{ kPa}$, $T=825$ and 925°C . P_{H_2} increases from 1.7 to 8.5 kPa, the total pressure from 3.4 to 10.2 kPa, α from 1 to 5 and Q from 160 to 480 sccm.

Two P_{H_2} domains are observed. For $P_{\text{H}_2} < 4 \text{ kPa}$ ($\alpha < 2.5$), hydrogen favours the deposition rate, the apparent reaction order with respect to H_2 being 2.5 at 825°C and 0.6 at 925°C . For higher H_2 partial pressures, the growth rate is no more influenced by this parameter.

Figure 4 : Growth rate variations with H_2 partial pressure for $P_{\text{MTS}}=1.7 \text{ kPa}$ and $Q=160\text{-}480 \text{ sccm}$

3.4- Influence of CH₄ partial pressure

Figure 5 represents the variations of the growth rate with the partial pressure of CH₄ (which is added to the initial gas mixture) for $P_{\text{MTS}}=1\text{kPa}$, $P_{\text{H}_2}=4\text{kPa}$. As P_{CH_4} is increased from 0.2 to 1 kPa, the total pressure increases from 5.2 to 6 kPa and the total flow rate from 200 to 240 sccm. If the addition of methane to the gas phase does not modify the growth rate for $T=925^\circ\text{C}$, a very slight decrease is observed at low temperature ($T=825^\circ\text{C}$).

Figure 5 : Growth rate variations with CH₄ partial pressure
for $P_{\text{MTS}}=1\text{kPa}$, $P_{\text{H}_2}=4\text{kPa}$ and $Q=200\text{-}240\text{sccm}$

3.5- Influence of HCl partial pressure

For $P_{\text{MTS}}=1\text{kPa}$, $P_{\text{H}_2}=4\text{kPa}$, $T=825$ and 925°C , the growth rate is drawn in figure 6 versus HCl partial pressure. For $T=925^\circ\text{C}$, HCl is added to the initial gas phase with a partial pressure rising from 0.15 to 0.5 kPa, which increases the total pressure from 5.15 to 5.5 kPa. For $T=825^\circ\text{C}$, P_{HCl} is raised from 0.05 to 0.1 kPa.

While at low temperature (825°C), additional HCl does not seem to influence the growth rate, for $T=925^\circ\text{C}$, an important inhibitor effect is observed with an apparent reaction order of -2.5. Nevertheless, as HCl content increases in the initial gas mixture, this inhibition decreases more and more.

Figure 6 : Growth rate variations with HCl partial pressure
for $P_{\text{MTS}}=1\text{kPa}$, $P_{\text{H}_2}=4\text{kPa}$ and $Q=200\text{-}220\text{sccm}$

4- ANALYSIS OF THE DEPOSIT

On the basis of X-ray diffraction, EPMA and EELS analyses, it has been shown that for $800 < T < 950^{\circ}\text{C}$ and $\alpha=5$, an increase of the total pressure from 5 to 20 kPa favours a silicon excess (60 - 70 Si at.%) and a very poor crystallization state. On the other hand, for $P=20\text{kPa}$ and $\alpha=5$, an increase of the temperature from 950°C to 1100°C favours a stoichiometric β -silicon carbide well crystallized with a high textural effect in the $\langle 111 \rangle$ direction. At last, for the low temperatures ($T < 950^{\circ}\text{C}$) and the low pressures ($P \leq 5\text{kPa}$), a decrease of the dilution ratio from 5 to 3 does not seem to modify the composition of the deposit which remains β -SiC.

5- DISCUSSION - KINETIC LAWS

The results presented in sections 3 and 4 permit to specify the kinetic process of pure SiC deposition from MTS/ H_2 system under conditions favourable to a rate control by the chemical reactions. Within the dilution ratio and total pressure range defined by $3 \leq \alpha \leq 5$ and $5 \leq P \leq 10\text{kPa}$, two temperature ranges are shown with different reactional mechanisms.

In the range of relatively low temperatures, a previous investigation of the gas phase by mass spectrometry analysis has evidenced a high activation energy of about $350\text{ kJ}\cdot\text{mol}^{-1}$ for the homogeneous decomposition of MTS [14], in accordance with the value reported by Burgess and Lewis for $P=100\text{kPa}$ and $700 \leq T \leq 850^{\circ}\text{C}$ [13]. For a temperature of about 825°C , the CVD process could be controlled by the MTS homogeneous decomposition. The apparent reaction order of 2.5 with respect to MTS is higher than that previously reported [13]. A zero-order is observed for the other species H_2 , CH_4 and HCl . As a result, the kinetic law for the formation of SiC can be written as follows for $3 \leq \alpha \leq 5$; $5 \leq P \leq 10\text{kPa}$ and $T \approx 825^{\circ}\text{C}$:

$$R = k_0 \exp(-E_a/RT) P_{\text{MTS}}^{2.5} \quad (1)$$

with $E_a > 300\text{ kJ}\cdot\text{mol}^{-1}$.

Due to this high order with respect to MTS, an increase of its initial partial pressure favours the homogeneous decomposition of MTS giving rise to reactive intermediate species, e.g. SiCl_2 or SiCl_3 as silicon source species, CH_3 as carbon precursor and HCl . Under these conditions of low temperature ($T \approx 825^{\circ}\text{C}$), for relatively low initial partial pressure of MTS, the extent of homogeneous decomposition is low and the deposition of SiC is kinetically controlled by the production of the actual source species such as SiCl_2 , SiCl_3 , CH_3 ... The growing surface is not saturated in chemisorbed species and the intermediates react on the surface more rapidly than they are formed in the homogeneous phase. As P_{MTS} is going on increasing ($1 \leq \alpha \leq 2$), reactive species are formed more and more rapidly, particularly HCl which is produced by both the homogeneous and heterogeneous reactions. The inhibitor chemisorption of Cl species can limit in this case the deposition rate, which possibly explains the important negative order of -3 observed for $P_{\text{MTS}} \geq 3\text{ kPa}$, as shown in figure 3.

For higher temperatures ($900 \leq T \leq 950^{\circ}\text{C}$), the activation energy (i.e. $160\text{ kJ}\cdot\text{mol}^{-1}$) is markedly lower than that for the MTS homogeneous decomposition. It means that this reaction is turned rapid and is no more limiting the SiC deposition process. Under the previously defined conditions, i.e. $3 \leq \alpha \leq 5$; $5 \leq P \leq 10\text{kPa}$ and $T \approx 925^{\circ}\text{C}$, the apparent reaction orders with respect to MTS, H_2 and CH_4 are zero (nil orders with respect to MTS and H_2 are in accordance with that obtained by Bessmann and Johnson[10]) and the order with respect to HCl is negative, varying from -2.5 to -0.6, which results in the following kinetic law :

$$R = k'_0 \exp(-E'_a/RT) \frac{1}{1 + P_{\text{HCl}}^n} \quad (2)$$

with $k'_0 = 5.10^5 \text{ mg min}^{-1} \text{ cm}^{-2} \text{ Pa}^n$, $E'_a = 160 \pm 40 \text{ kJ.mol}^{-1}$ and $2.5 \leq n \leq 0.6$.

This kinetic behaviour shows that the MTS dissociation has provided enough reactive intermediates to saturate the surface. The inhibition effect of HCl, in accordance with Besmann et al. results [11], which decreases as P_{HCl} raises, confirms the heterogeneous limitation of the overall kinetic process. The decrease of the growth rate when P_{MTS} increases above 3 kPa can also be explained on the basis of inhibitor chemisorption of Cl species favoured by increasing the total pressure.

CONCLUSION

This work is a first approach to the kinetic laws of SiC vapour deposition from $\text{CH}_3\text{SiCl}_3\text{-H}_2$ precursors, determined in specific ranges of temperatures, total pressures and dilution ratios. For each chemically controlled domain, the limiting step and a set of kinetic data have been derived. A more advanced paper with tentative mechanisms fitting the given kinetic laws will follow.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. S. Schamm (CEMES-LOE, CNRS, Toulouse) for her contribution to the EELS analyses and both DRET (French Ministry of Defense) and SEP for their financial support through a grant to F.Loumagne.

REFERENCES

- 1- J. SCHLICHTING, Powder Metall. Int., 12, 3 (1980) 141 and 12, 4 (1980) 196.
- 2- K. MINATO and K. FUKUDA, J. Nucl. Mater., 149 (1987) 233.
- 3- P. TSUI and K.E. SPEAR, Mat. Sci. Res., 17 (1984) 371.
- 4- M.G. SO and J.S. CHUN, J. Vax. Sci. Technol., 6 (1988) 5.
- 5- K. BRENNFLECK, E. FITZER, G. SCHOCH and M. DIETRICH, Proc. 9th Int. Conf. on CVD, Pennington, Mc D. Robinson et al., eds., The Electrochem. Soc. (1984) 649.
- 6- R. FEDOU, F. LANGLAIS and R. NASLAIN, J. Mat. Synth. and Proc., 1, 1 (1993).
- 7- R. FEDOU, F. LANGLAIS and R. NASLAIN, J. Mat. Synth. and Proc., 1, 2 (1993).
- 8- L.M. IVANOVNA and A.A. PLETIOUCHKINE, Izvest. Akad. Nank. SSSR, Neorg. Mater. 4, 7 (1968) 1089.
- 9- T.M. BESMANN, B.W. SHELDON and M.D. KASTER, Surf. Coat. Technol., 43/44 (1990) 167.
- 10- T.M. BESMANN and M.L. JOHNSON, Proc. Int. Symp. on Ceramic Materials and Components for Engines (Las Vegas, NV, 1988), V.J. Tennery, ed., Am. Ceram. Soc., Westerville, OH, 1989.
- 11- T.M. BESMANN, B.W. SHELDON, T.S. MOSS III and M.D. KASTER, J. Am. Ceram. Soc., 75, 10 (1992) 2899.
- 12- F. LANGLAIS and C. PREBENDE, Proc. 11th Int. Conf. on CVD, K.E. Spear and G.W. Cullen, eds., The Electrochem. Soc., Pennington, (1990) 686.
- 13- J.N. BURGESS and T.J. LEWIS, Chem. Ind. (1974) 76.
- 14- F. LOUMAGNE, F. LANGLAIS and R. NASLAIN, to be published.