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Simulation of Chemical Vapour Deposition of SiC from Methyltrichlorosilane in a Hot Wall Reactor

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Abstract: A two-dimensional simulation for the deposition of SiC from gas mixtures containing MTS-H₂-HCl-Ar was set up on the basis of the commercial CFD-code PHOENICS (1.6.6). Previously measured rate equations [1] that describe the deposition reaction were implemented. Allowing deposition on all surfaces in the reactor the model takes into account the influence of local depletion of MTS and enrichment of HCl during deposition also upstream of the substrate. In the range from 800 to 1400 °C the calculated total mass increase rates on the substrate as a function of temperature, partial pressure and flow rate show good agreement with experiments. The simulation model was then used to calculate local deposition rates with the aim of finding suitable conditions to produce uniform layer thickness.

1. INTRODUCTION

Production of SiC coatings and SiC matrix composites using chemical vapour deposition (CVD) is a well introduced technology. One possible reactant currently used in commercial operations is methyltrichlorosilane (MTS) in the presence of H₂ [2, 3, 4, 5]. Especially in the case of chemical vapour infiltration (CVI) the knowledge of appropriate process parameters is required to achieve good infiltration and low residual porosities. In-advance calculation of the local deposition rates is therefore of particular interest.

Deposition rates are often determined in a complex way by interaction of both gas phase and surface reactions and transport processes. In order to describe the transport phenomena computational fluid dynamic codes have gained increasing importance in recent years. Modelling of the chemistry is usually done assuming local thermodynamic equilibrium or kinetically limited reaction rates. Simulation of CVD processes considering transport phenomena combined with chemistry modelled by kinetically limited rate equations were carried out for the deposition of e.g. silicon, gallium arsenide and tungsten [6, 7, 8, 9].

In the case of deposition of SiC from MTS the formulation of local thermodynamic equilibrium showed to be of little relevance for the description of the deposition process. In this system modelling of gas phase and heterogeneous chemistry by rate equations has been carried out by several research groups [10, 11, 12, 13]. Results for modelling the homogeneous gas reactions give the order of magnitude of the reaction rates. The modelling of heterogeneous reactions is even more difficult so that quantitative prediction of the deposition rate is still not possible.

In the present work a simulation of the SiC deposition rate is presented which makes use of rate equations describing the deposition reaction as determined previously in this laboratory [1]. The rate equations are implemented in the CFD code PHOENICS (1.6.6). With these equations and the description of the transport processes in the gas phase the simulations showed good agreement with experimental observations in wide ranges of operating parameters. In this state of modelling it proved unnecessary to include the calculation of thermodynamic equilibrium.

2. EXPERIMENTAL REFERENCE

The simulation is based on experimental results obtained previously in this laboratory [1]. The deposition rate of SiC was measured with a magnetically coupled themobalance as described before [14, 15]. The reactor geometry used for experiments and simulation is given in [Fig. 1](#). The experimental conditions are summarized in [Table 1](#).

Table 1: Experimental conditions for SiC deposition

Feedgas mixture:	0,9 - 8,1 % CH_3SiCl_3 0,9 - 8,1 % H_2 0,0 - 0,7 % HCl balance Ar	(methyltrichlorosilane = MTS) with $[\text{H}_2]/[\text{MTS}] = 1$
Reactor type:	Vertical tubular hot wall,	
Flowrate:	100 - 200 $\text{l}_{\text{STP}}/\text{h}$, atmospheric pressure	
Temperatures:	800 - 1400 °C	
Substrate:	Graphite plates, 10 x 50 x 2 mm^3	
Solid product:	β - SiC	

A reaction order of 1 for MTS and an apparent activation energy of 380 kJ/mol was found. With respect to HCl two different reaction orders were found:
-1 in the region of $[\text{MTS}]/[\text{HCl}] > 5,8$ and -3 in the region of $[\text{MTS}]/[\text{HCl}] < 5,8$.

3. SIMULATION

A model was set up on the basis of the commercial CFD-code PHOENICS (Version 1.6.6) in order to simulate the steady state reactor operation by numerical integration of the partial

differential equations for conservation of mass, heat, momentum and species.

3.1 Properties

Viscosity, heat capacity and thermal conductivity data for pure substances as a function of temperature were taken from the DIPPR data bank [16]. The corresponding properties for the gas mixtures and the multicomponent diffusion coefficients were calculated following well established methods of kinetic theory [17]. The actually employed methods are listed elsewhere [18]. For economy in computing time the following simplifications were made: The heat capacity c_p was calculated from feedgas composition rather than from local composition. The Diffusion coefficients D were handled in PHOENICS in form of a Schmitt number $Sc = \eta / (\rho \cdot D)$ and the thermal conductivity λ is made available to

PHOENICS in form of a Prandtl number $Pr = (\eta \cdot c_p) / \lambda$. Both Sc and Pr were calculated from the feedgas composition and feedgas temperature and subsequently treated as constants. Due to the opposing influence of temperature on the properties which effect the Schmitt- and Prandtl numbers the deviation of this procedure from locally calculated values does not exceed 5 % in the case of Sc and 25 % in the case of Pr .

The density ρ was calculated according to the ideal gas law. For all conditions investigated flow could be assumed to be laminar and buoyancy forces could be neglected.

3.2 Geometry and grid

The geometry of the reactor being axisymmetric a two-dimensional model was set up. Calculations were carried out for a cylindrical substrate of the same length and surface area as the original rectangular substrate. For the simulation a grid was fitted to the reactor geometry with the size of the cells being reduced in the vicinity of solid surfaces. Results proved to be grid independent with 32 cells in radial and 72 cells in axial direction.

3.3 Boundary conditions

Along the boundary at the symmetry axis of the reactor tube the radial gradients of velocity, concentration or temperature were taken as zero.

Fig. 1: Schematic of reactor geometry

3.3.1 Energy

At reactor and substrate walls a constant parabolic temperature profile in axial direction was assumed based on experimental data. At the reactor inlet and outlet the temperature was set to 25 °C and no axial gradients were assumed. Heats of reaction were neglected.

3.3.2 Mass and momentum

At the reactor inlet a constant feedgas flow rate was prescribed, the pressure at the reactor outlet was taken as 1 bar. No slip was assumed for the velocity components.

3.3.3 Species and chemical reactions

Constant inlet concentrations were prescribed for all species, at the outlet no axial gradients were assumed. The species balanced were MTS, HCl and H₂. Gas phase reactions were not taken into account. The only chemical reaction accounted for in the model is the heterogeneous deposition reaction

taking place on solid surfaces, either reactor wall or substrate. Its rate was taken from experimental measurements [1] which delivered two rate equations, where brackets denote concentrations:

$$\begin{aligned} j_{\text{SiC(I)}} &= k_I [\text{MTS}] [\text{HCl}]^{-1} \exp(-A_I/RT) \quad \text{for region I at } [\text{MTS}]/[\text{HCl}] > 5,8, \\ \text{and} \\ j_{\text{SiC(II)}} &= k_{II} [\text{MTS}] [\text{HCl}]^{-3} \exp(-A_{II}/RT) \quad \text{for region I at } [\text{MTS}]/[\text{HCl}] < 5,8 \end{aligned}$$

The activation energies A_I and A_{II} were experimentally determined to be equal amounting to about 380 kJ/mol.

For the present simulation it has been assumed that these two rate equations describe two consecutive steps of the deposition reaction of which the slower one is rate-determining. Therefore, the rates $j_{\text{SiC(I)}}$ and $j_{\text{SiC(II)}}$ were calculated for each set of conditions (temperature, [MTS] and [HCl]) and the lower values obtained in each case were used as the actual deposition rates. Calculations showed that modification of the activation energy of 380 kJ/mol to $A_I = 420$ kJ/mol and $A_{II} = 385$ kJ/mol including the respective adaptation of k_I and k_{II} yielded better agreement between simulation and experiment.

3.4 Solution procedure

Solution was achieved calculating slab-by-slab with the built-in linear equation solver. Convergence for species conservation was judged by the whole field residual sums (normalized by the maximum value and number of grid points) being less than 10^{-8} and by checking the global mass balances. Results were accepted with a mass balance error less than 0.2 %.

3.5 Results

Figures 2 - 5 show simulation results together with experimental observations [1]. Here deposition rate is expressed as the mass increase rate integrated over the total surface of the substrate. In Fig. 4 the symbols marked with an arrow give experimental deposition rates obtained with $p_{\text{HCl}} = 0$ in the feedgas. Also the curve for the simulated deposition rates is extended to the values for $p_{\text{HCl}} = 0$ in the feedgas (dashed line).

Fig. 2: Temperature influence on deposition rate at 150 l_{STP}/h flow rate and $p_{\text{HCl, feed}} = 0$, $p_{\text{MTS, feed}} = 17,9$ mbar

Fig. 3: MTS influence on deposition rate at 150 l_{STP}/h flow rate and $p_{\text{HCl, feed}} = 0$

Fig. 4: HCl influence on deposition rate at 150 l_{STP}/h flow rate and $p_{\text{MTS, feed}} = 17,9$ mbar

Fig. 5: Total flow rate influence on deposition rate at $p_{\text{MTS, feed}} = 17,9$ mbar

Figures 6 and 7 show simulated results for the local deposition rates along the substrate. Partial pressures of HCl at the upstream (0 mm) and downstream end (50 mm) of the substrate are given to show the strong connection between deposition rate and local HCl concentration. MTS partial pressures at the downstream end of the substrate are given to show the degree of MTS depletion, starting from 17,9 mbar in the feedgas. Fig. 6 describes the local deposition rates for gas mixtures initially free of HCl, and Fig. 7 gives examples for gases with increasing HCl contents in the feedgas: The absolute deposition rates decrease strongly, but the local rates vary much less along the length of the substrate.

Fig. 6: Simulated local deposition rate along substrate at 150 l_{STP}/h flow rate and P_{MTS, feed} = 17,9 mbar, P_{HCl, feed} = 0

Fig. 7: Simulated local deposition rate along substrate at 150 l_{STP}/h flow rate and P_{MTS, feed} = 17,9 mbar at different HCl concentrations in the feedgas

4. DISCUSSION

Fig. 2 shows that for temperatures up to 1150 °C and for feedgases free of HCl agreement of simulation with experiment is very close. Also excellent agreement is found for the influence of total flow rate for feedgas free of HCl at both high and low temperatures (Fig. 5). MTS depletion during the process reaches some 15 % at the end of the substrate for deposition at 1047 °C (Fig. 6). From Fig. 3 can be seen that the simulation model is capable to describe the effect of MTS variations over a much wider range than that caused by consumption. The cases given in Fig. 2 and 3 always include consideration of the retarding effect of HCl developed in situ. Fig. 4 shows the influence of HCl amounts already added to the feedgas mixture. For deposition at 850 °C and up to P_{HCl} = 4,7 mbar in the feedgas the reaction rate at the substrate is governed by rate equation (I). HCl partial pressures higher than 4,7 mbar lead to a deposition along the substrate governed by rate equation II. This is indicated by the steeper gradient of the curve. For deposition at 900 °C (Fig. 4 and 7) transition from rate equation (I) to rate equation (II) at the substrate occurs between P_{HCl} = 2,7 and 3,6 mbar in the feedgas.

Fig. 6 illustrates the effect of HCl developed in situ retarding the deposition rate. The deposition rates at the upstream and downstream ends of the substrate vary by a factor of 2,5 .. 3 at all temperatures. Fig. 7 shows that these effects of HCl enrichment on the local variation of deposition rate decrease with HCl additions to the feedgas. The curves for HCl partial pressures in the feedgas being equal or higher than 2,7 mbar exhibit the dominating influence of the parabolic temperature profile on the deposition rate along the substrate. Unfortunately this higher uniformity in deposition is related to a much lower deposition rate.

In spite of the simple approach chosen to describe the deposition reaction the simulation shows good agreement with the experimental observations. The deviations observed may to a greater part be due to the simplifications made in describing the reaction chemistry.

5. CONCLUSION

The deposition of SiC from gas mixtures containing MTS-H₂-HCl-Ar was simulated. In the simulation model the chemical reaction is accounted for by two rate equations describing the local SiC deposition rate as a function of temperature and the concentrations of MTS and HCl. These rate equations for local deposition of SiC were derived from mass increase rates integrated over the total surface of a 50*10*2 mm³ substrate (integral deposition rates) [1]. The reaction rate equations together with modelling of transport in multicomponent gas mixtures [18] were implemented to the CFD code PHOENICS (1.6.6). The simulated deposition rates of SiC were found in good agreement with experiments over a wide range of deposition parameters. Furthermore it was shown that a very simplified description of the deposition chemistry in combination with gas transport modelling was already able to yield good simulation results. The assumption of the two rate equations describing two consecutive steps in the deposition reaction proved to be justified. With the incorporation of appropriate modelling of porosity an application of this simulation model to CVI processes appears to be feasible.

Deviations of simulation from experiment indicate that for a better agreement the description of the deposition chemistry should be expanded and include e.g. homogeneous gas phase reactions.

The simulations showed, that the obstructing effect of HCl on deposition uniformity decreased with HCl additions to the feedgas. Special advantage of this modified process is seen in the area of chemical vapour infiltration and coating of complex geometries. An alternative to obtain better uniformity of deposition might be the use of chlorine-free precursor systems.

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