Local Deposition Rates of α-Al_2O_3 from $AlCl_3$-CO_2-H_2-HCl derived with PHOENICS-CVD from Thermogravimetric Measurements in a Hot-Wall Reactor with long Isothermal Zone

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Uniform coating of substrates with complex geometry requires detailed knowledge of the deposition rate as a function of partial pressures, temperature, flow rate, residence time in the hot zone and location of the sample in the reactor. The objective of this numerical simulation based on experimentally determined reaction rates is the description of the chemical vapor deposition (CVD) process of α-Al_2O_3 and the prediction of local deposition rates to achieve coatings of uniform thickness.

α-Al_2O_3 may be deposited from a variety of different precursors, but in most industrial applications $AlCl_3/H_2/CO_2$ gas mixtures are used (1-5). Especially the product gas HCl is of great interest because is shows a strong retarding effect on the deposition of α-Al_2O_3 which was shown by Schierling et al. (6). Great efforts have been reached in describing elementary homogeneous reactions in the system $AlCl_3/H_2/CO_2$ (7) and also in ab-initio calculation of thermodynamic and kinetic data (8,9), but there is still a lack of elementary kinetic data describing heterogeneous reactions during CVD of α-Al_2O_3 (7). For this reason experimental measurements on the reaction kinetics of α-Al_2O_3 have been conducted varying systematically the inlet partial pressures of each species, temperature, total volumetric flow and position of the samples within the long isothermal zone of the CVD furnace which means a variation of the residence time of the gas mixture. The results from these measurements have been taken to describe the overall deposition process by an Arrhenius type equation. On the basis of this empirical kinetic equation, calculations of local deposition rates have been carried out using the CFD program PHOENICS-CVD (10,11).

Thermogravimetric rate measurements have been carried out on the deposition of α-Al_2O_3 from $AlCl_3$-CO_2-H_2-HCl-Ar mixtures at 100 mbar and 900...1200°C in a vertical hot-wall CVD reactor with a 450 mm isothermal zone. Neglecting the first monolayers and reactions with the substrate, the CVD of α-Al_2O_3 is the deposition of alumina on alumina. Consequently, to investigate the deposition kinetics of this process, we have chosen substrates from thin alumina foils (Keral 96). The measurements were conducted at different positions within the 450 mm long isothermal zone to investigate the influence of residence time while all other parameters were kept constant.

To describe the measured overall deposition rate in the PHOENICS-CVD simulations, a semi-empirical Arrhenius type equation for the chemical vapor deposition of alumina was set up as follows:

$$j(Al_2O_3) = k\cdot\exp(-E_A/RT)\cdot[CO_2]^a\cdot[AlCl_3]^b\cdot[H_2]^c\cdot[HCl]^d.$$

In this equation it is assumed that one of the steps in the deposition mechanism is rate limiting and that all other steps are in equilibrium. The constants "a-d" represent measured reaction orders and "E_A" apparent activation energies. The factor "k" represents the frequency factor and was adapted so that the calculated integral deposition rates agree well with the experimental results.

The calculated integral deposition rate dependencies of the partial pressures of $AlCl_3$, H_2 and CO_2 including the retarding effect of HCl could be well described by the empirical relationship with the parameters chosen from the experiments. The dependencies of the deposition rates on temperature and the volumetric flow rate still are not completely satisfactory.

The experimental data were used in the PHOENICS-CVD software package to predict local deposition rates and to define conditions for highly uniform alumina deposition. Calculations of the local deposition rates with the same parameters as used to reproduce the kinetic measurements have been carried out for both the plain substrates located in the axis of the reactor and the hot wall of the reaction tube, which represents the deposition over the whole temperature profile of the CVD reactor. The results will be presented and discussed in the complete manuscript.

To obtain homogeneous layers with good yield for the given reactor geometry, a total pressure of 100 hPa, a total gas flow of 20 slh, a deposition temperature of 1050°C and a gas mixture containing 1.3 % $AlCl_3$, 12 % CO_2, 60 % H_2 and at least 4 % additional HCl is recommended.

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