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MATERIALS & MANUFACTURING PROCESSES, 8(3), 315-329 (1993)

THIN ALUMINA AND SILICA FILMS BY CHEMICAL VAPOR DEPOSITION (CVD)

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ABSTRACT

Alumina and silica coatings have been deposited by MOCVD (Metal Organic Chemical Vapor Deposition) on alloys to protect them against high temperature corrosion. Aluminium Tri-Isopropoxide (ATI) and DiAcetoxyDitertiaryButoxySilane (DADBS) have been used as metal organic precursors to prepare these ceramic coatings. The influence of several process steps on the deposition rate and surface morphology is discussed. The deposition of SiO_2 at atmospheric pressure is kinetically limited below 833 K and is a mixed first and second order reaction with an activation energy of 155 $kJ.mole^{-1}$. The deposition of Al_2O_3 is kinetically limited below 673 K and is a first order reaction with an activation energy of 30 $kJ.mole^{-1}$ at atmospheric pressure. The deposition of Al_2O_3 is kinetically limited below 623 K and is a second order reaction at low pressure (3 torr) with an activation energy of 30 $kJ.mole^{-1}$. The decomposition of both precursors involves a β-hydrogen elimination reaction by which DADBS decomposes to acetic acid anhydride, 2-methyl propene, SiO_2 and H_2O, while ATI decomposes to 2-propanol, propene, Al_2O_3 and H_2O.

INTRODUCTION

The interest in ceramic coatings has recently increased. These coatings are used to increase wear and corrosion resistance of base materials, but are mostly used for optical and electrical device fabrication. In the last two fields, where highly pure coatings are required, CVD has become a very popular coating technique and an enormous number of papers has been published concerning the characterization of these coatings. The number of papers concerned with the CVD process itself is far less, although some good reviews are available (1,2,3). Van Brekel (1) introduced a model to explain the deposition rate and the surface morphology as a function of the

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reaction temperature. This model is based on chemical reactions and transport of reactants and products and nowadays still the base of all other models describing CVD processes.

Next to the best known Atmospheric Pressure (APCVD) and Low Pressure Chemical Vapor Deposition (LPCVD) techniques, modified CVD-techniques have been used. These techniques have other activation sources to start the chemical reaction of the precursors than thermal heating. The substrate temperature will then be lowered and unwanted side reactions of the substrate are avoided. Examples of these techniques are Plasma Enhanced (PECVD), Laser (LCVD), Electron Beam (EBCVD) and Microwave (MCVD) Chemical Vapor Deposition. Metal Organic Chemical Vapor Deposition (MOCVD) has also been used to reduce the deposition temperature. This technique is based on the fact that metal organic precursors are highly instable and therefore coatings are formed at reasonably low temperatures.

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In this work the synthesis of alumina and silica films by MOCVD is described. The processing of MOCVD coatings is almost identical to that of APCVD and LPCVD coatings. Gas phase reactions preliminary to the deposition reaction have been included in this model. The models used in this work can be applied to APCVD, LPCVD and MOCVD. The protective properties of the coatings are not considered here, but published elsewhere (4,5).

THEORY

The study of the CVD process is based on thermodynamics and kinetics. Thermodynamic studies give information on whether the precursors react to the desired coating, while kinetic studies give information about the deposition rate. Thermodynamic calculations have mostly been performed with computer programs like SOLGASMIX (6), but are hardly possible for MOCVD processes, due to a lack of thermodynamic data of MO-compounds. Furthermore it should be pointed out that kinetic theories, concerning MOCVD, are always based on curve fitting instead of on modelling of molecular processes, because the number of possible reaction steps is very large.

Most MOCVD processes have been performed in a plug flow reactor. In this type of reactor the MOCVD process can be divided in several process steps involving transport and reaction (Fig.1):

- Supply of evaporated reactant(s) by an inert gas stream
- Gas phase reactions
- Diffusion of reactants or intermediates from the gas through a stagnant boundary layer to the surface
- Adsorption of the reactants or intermediates on the surface
- Chemical reactions on the surface, resulting in the desired product layer and some by-products
- Desorption of by-products

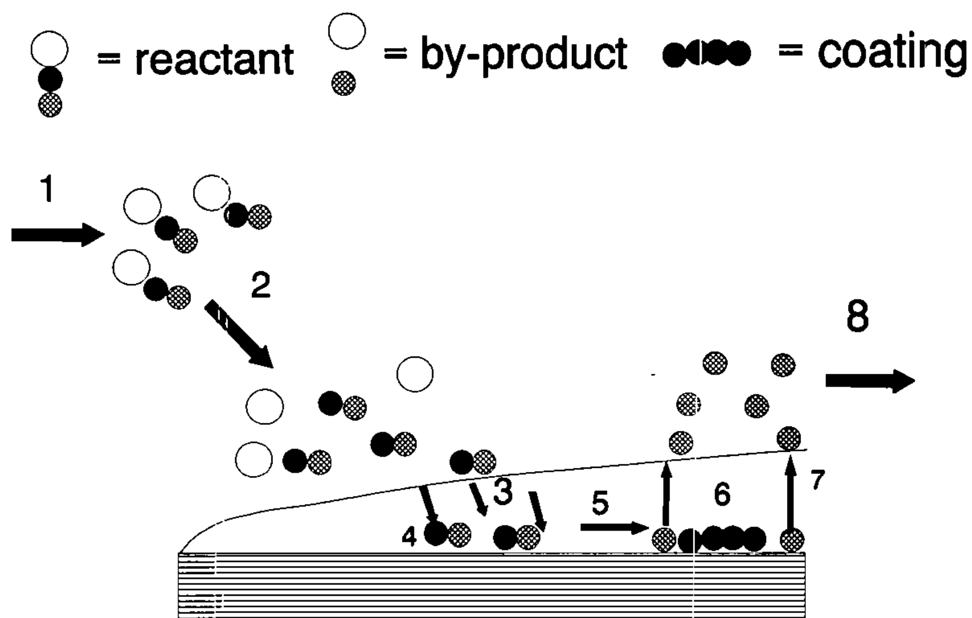

Figure 1. Schematic model of the CVD process (see text)

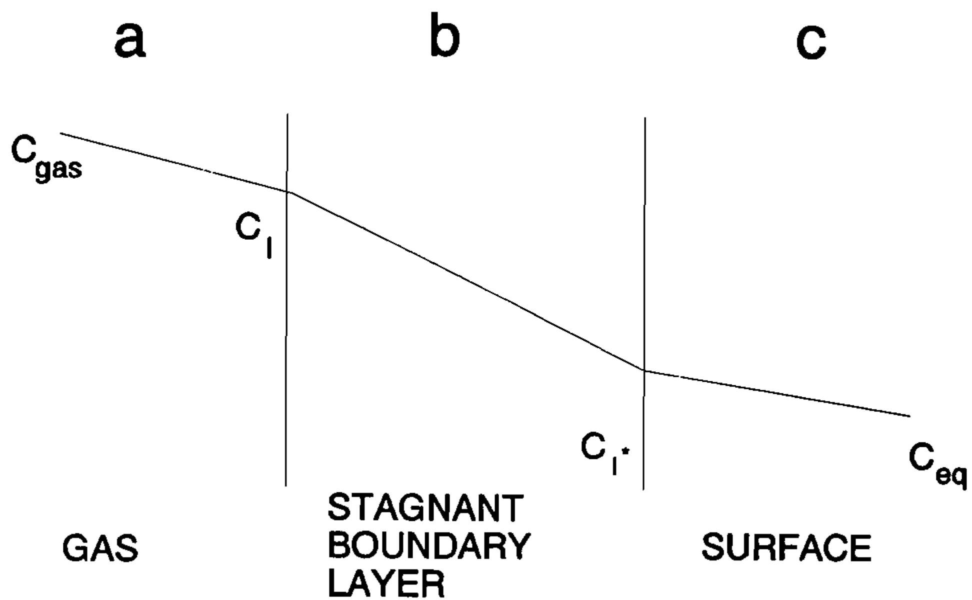

Figure 2. Schematic representation of the stagnant boundary layer model, in which gas phase (region a) and surface reactions (region c) and diffusion through the stagnant boundary layer (region b) occur.

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- Diffusion of by-products from the surface through the stagnant boundary layer to the gas phase
- Removal of by-products and unreacted species

The slowest step in this reaction sequence determines not only the overall reaction (= deposition) rate, but it can also influence the surface morphology. From this fact, it can be concluded that knowledge about every step is necessary to produce a coating with the desired properties.

Steps 1 and 8 can easily be manipulated by adjusting the total flux and are therefore not assumed to be rate limiting. In the first part of this section, the diffusion across the stagnant boundary layer and the chemical reactions are discussed, while rate limitation by ad/desorption reactions is discussed in the last part of this section.

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When reaction and/or diffusion processes are considered to be rate limiting, three concentration gradients can be observed: one in the gas phase (caused by gas phase reactions), one across the stagnant boundary layer (due to the diffusion processes) and one on the surface (due to surface reactions) (Fig.2). An accumulation of species will be caused by the slowest process and the concentration gradient caused by that process will be larger than all others.

The diffusion flux can be calculated from Fick's first law:

$$J_{B.L.} = \frac{D}{\delta}(c_1 - c_{1^*}) \tag{1}$$

The chemical reaction rates in the gas phase (2a) and on the substrate (2b) can be described by:

$$r_{gas} = k_1 (c_R - c_1)^n \tag{2a}$$
$$r_s = k_2 (c_{1^*} - c_{eq})^m \tag{2b}$$

When both reactions are assumed to be first order in c_R and c_{1^*}, the combination of equation (1) and (2) leads to:

$$\frac{c_R - c_1}{c_1 - c_{1^*}} = \frac{D}{k_1\delta} = \frac{1}{Sh_1} \tag{3a}$$
$$\frac{c_{1^*} - c_{eq}}{c_1 - c_{1^*}} = \frac{D}{k_2\delta} = \frac{1}{Sh_2} \tag{3b}$$

In this equation $(k\delta)/D$ is the dimensionless Sh(erwood) number. From these equations two limiting situations can be recognized:

1. If Sh << 1, the concentration gradient across the stagnant boundary layer is almost zero, i.e., the growth rate is limited by the chemical reaction.

2. If Sh >> 1, the concentration gradient across the stagnant boundary layer is larger than the other gradients and the growth rate is limited by the diffusion through this layer.

(MO)CVD processes are reaction limited at low temperatures, and at higher temperatures the diffusion is rate limiting (1) (Fig.3). Coatings produced under diffusion limiting conditions have an inhomogeneous layer thickness, due to the fact that the thickness of the stagnant boundary layer is a function of the flow pattern around the substrate and its surface condition. Coatings, formed under the reaction limiting condition, have a uniform coating thickness (5).

In the reaction limited regime, gas phase (left part equation 4) or surface reactions (right part equation 4) can be rate limiting:

$$R \xrightarrow{k_1} I \xrightarrow{k_2} P \qquad (4)$$

The consumption rate of the reactants can be given by:

$$\phi \frac{\partial C_R}{\partial x} = -k_1 . C_R \qquad (5)$$

The reaction rate of the intermediate is given by:

$$\phi \frac{\partial C_I}{\partial x} = -k_2 C_I + k_1 C_R \qquad (6)$$

While the rate of product formation is given by:

$$\phi \frac{\partial C_P}{\partial x} = k_2 \, C_I \qquad (7)$$

In these equations, influences of thermal gradients and transport in the reactor by diffusion are neglected, while the reactions are assumed to be first order. The reactant, intermediate, and product concentration and the position in the reactor are normalised, i.e., $C_R = c_R/c_{R0}$, $C_I = c_I/c_{R0}$ and $C_P = c_P/c_{R0}$ ($C_A + C_I + C_P = 1$) and $x = l/l_0$. In Fig.4, the calculated concentration gradient profiles of the intermediate are given for different k_1/k_2 ratios. When k_1 is large compared to k_2 the intermediate formation can be neglected.

At concentrations above a critical value the adsorption and desorption rates of reactants and by-products become rate limiting, i.e., the surface becomes covered with

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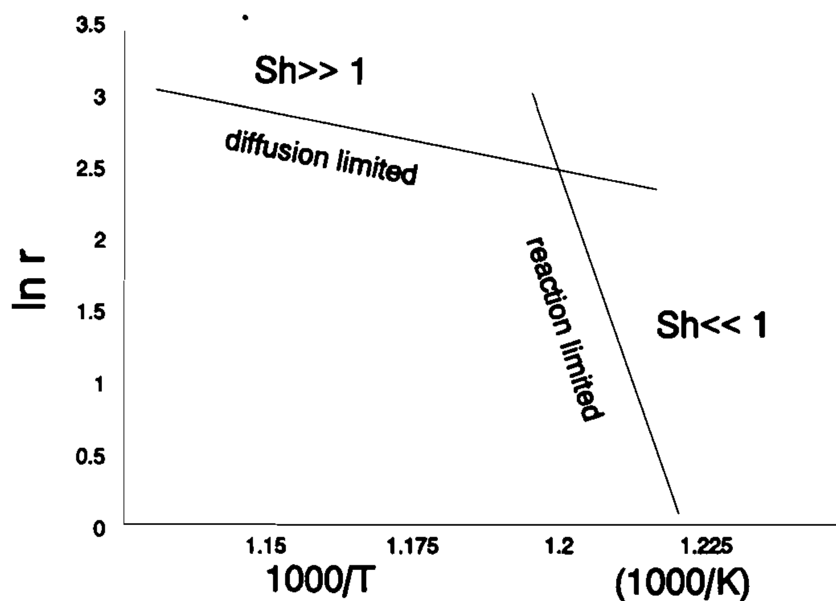

Figure 3. A theoretical Arrhenius plot of a CVD process in which diffusion (at high temperatures) and chemical reactions (at low temperatures) are rate limiting.

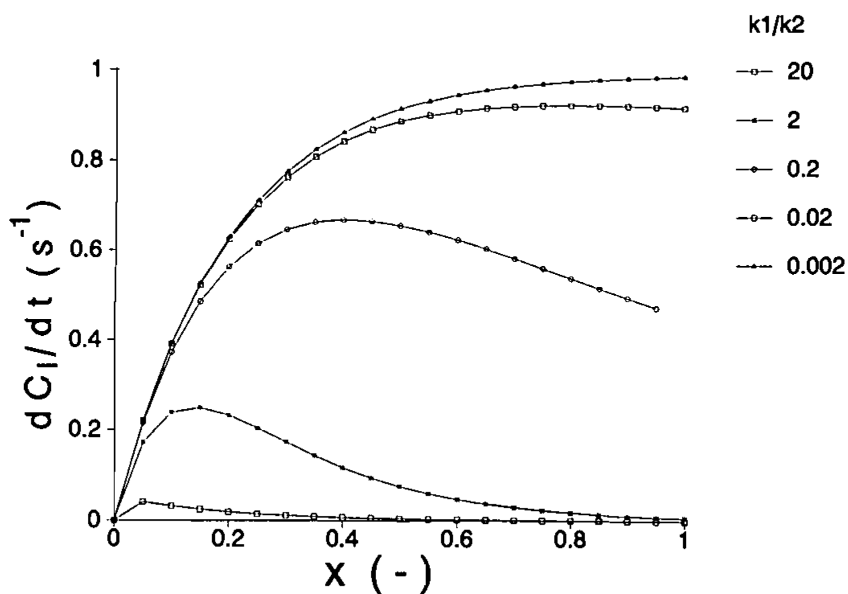

Figure 4. Theoretical profile of intermediate species in a tube furnace for different k-ratios for two serial first order reactions.

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those species. The rates of adsorption and desorption are, according to Langmuir, given by:

$$r_{ads} = k_{ads}\, c_I\, (1-\Theta) \tag{8}$$

$$r_{des} = k_{des}.\Theta \tag{9}$$

When these reactions are in equilibrium the surface coverage (Θ) can be calculated by:

$$\Theta = [I_s] = \frac{b.c_I}{b.c_I + 1} \tag{10}$$

This relation, in which the adsorption constant $b = k_{ads} / k_{des}$, can be combined with the rate equation of the surface reaction:

$$r_{dep} = k_{dep}.[I_s] = \frac{k_{dep} b.c_I}{b.c_I + 1} \tag{11}$$

As can be seen from Fig.5, the reaction rate in the high concentration regime becomes constant ($r_{dep} = k_{dep}$).

EXPERIMENTAL

The MOCVD experiments were carried out either in a reactor at atmospheric pressure (Fig.6) or in a low pressure reactor (Fig.7). The Metal Organic precursors Aliminium Tri Isopropoxide (ATI) to produce Al_2O_3 coatings and DiAcetoxy Ditertairy-ButoxideSilane (DADBS) to produce SiO_2 coatings are partially evaporated in a saturator vessel, which is kept at a constant temperature by an oil bath. A nitrogen gas stream (carrier gas) is passed through the saturator to transport the vapor to the reactor. Before the vapor stream enters the reactor it can be mixed with an extra amount of nitrogen gas (diluting gas) to reduce the vapor concentration. The furnace temperature is controlled by thermocouples which are placed inside the reaction tube. Unless stated otherwise, the temperature of the oil bath, the reactor pressure, the furnace temperature, and the flows of the diluting and carrier gas were kept constant during the experiments as given in Table 1.

Incoloy 800 H was used as substrate during deposition experiments. Prior to deposition this alloy has been polished on 25, 6, 1 and 0.25 μm diamond paste and etched in a 5% 3M HNO_3 / 95% ethanol (P.A.) solution. The products of the decomposition reactions were monitored by a Mass spectrometer (SpectraMass) to obtain information about the decomposition chemistry of DADBS and ATI.

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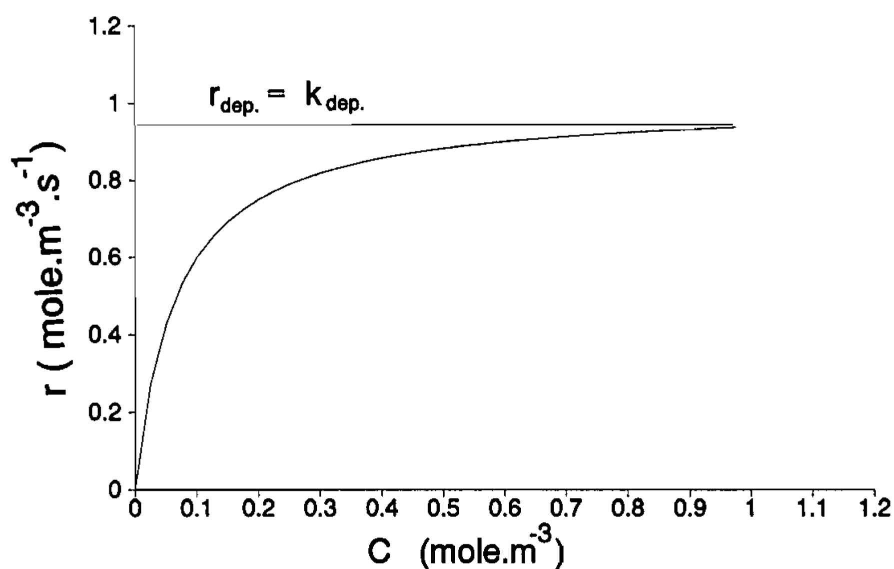

Figure 5. The reaction rate according to Langmuir model. At low concentrations a normal first order relation is observed, while at higher concentration the reaction rate becomes constant due to surface limitation.

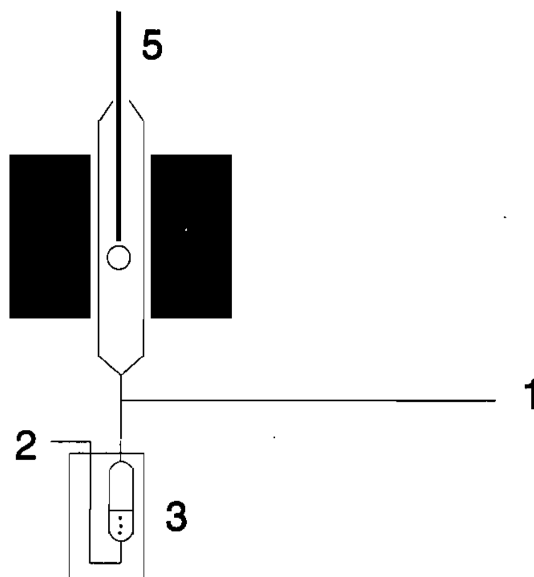

Figure 6. Schematic drawing of the atmospheric MOCVD-equipment. (1) nitrogen diluting gas, (2) nitrogen carrier gas, (3) evaporation vessel at constant temperature with metal organic precursor, (4) furnace, and (5) thermocouple with specimen.

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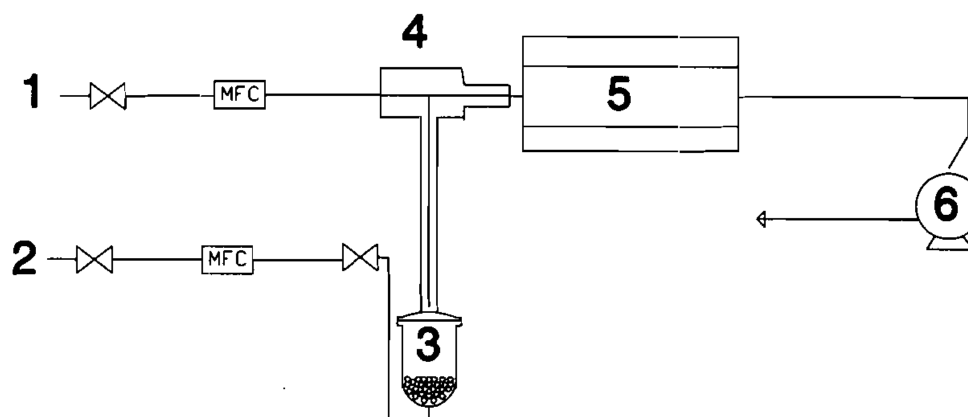

Figure 7. Schematic drawing of the low-pressure MOCVD-equipment. (1) nitrogen diluting gas, (2) nitrogen carrier gas, (3) evaporation vessel at constant temperature with metal organic precursor, (4) mixing chamber, (5) 3-zone furnace, and (6) vacuum pump.

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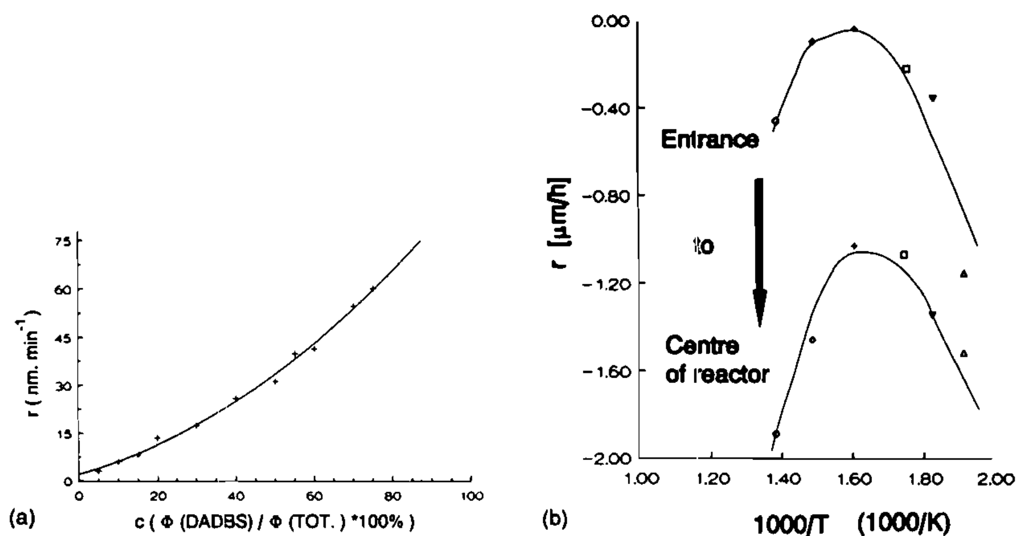

Figure 8. Measured Arrhenius plots of the deposition rate of SiO_2 from DADBS (a) and Al_2O_3 from ATI (b).

RESULTS AND DISCUSSION

Determination of the Kinetic Regimes

The analysis of the MOCVD process starts with the determination of the diffusion and reaction limited regimes, since for most applications only films with a uniform thickness can be used, and therefore the MOCVD process must be operated under reaction limited conditions. For both Al_2O_3 deposition from ATI and SiO_2 from DADBS, Arrhenius plots were determined (Fig.8). The deposition of SiO_2 with DADBS as a precursor is in agreement with the above described theory. From the reaction limited regime the activation energy of the chemical reaction is determined to be 150 $kJ.mole^{-1}$. The optimum deposition temperature (= highest reaction rate in reaction limited regime) for the SiO_2-process is about 833 K. The results of ATI are more complicated, since the reaction rate at the highest temperatures decreases, which can be explained by the fact that the intermediate concentration decreases by gas phase polymerisation (= powder formation). The activation energy for the decomposition reaction of ATI is 30 $kJ.mole^{-1}$. The decomposition of ATI is kinetically limited below 673 K at atmospheric pressure and below 623 K at low pressure (3 torr).

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Determination of the Reaction Order

Once the reaction limited regime is determined, the chemical reaction rate at constant temperature can be optimised by changing the concentration of the MO-compound in the gas stream. In general, the rate of each chemical reaction at a constant temperature is given by:

$$r = -k.c^n \quad (12)$$

For an accurate prediction of the reaction rate for each concentration the reaction order n is important. This order is often determined by using a double logarithmic plot of the reaction rate versus reactant concentration:

$$\ln r = \ln k + n.\ln c \quad (13)$$

As can be seen from Fig.9, the SiO_2-deposition rate has an increasing reaction order from 1 in the low concentration area to 1.6 in the high concentration area. This phenomenon may be explained by assuming that two different parallel reactions, one first order and one second order gas phase reaction are rate limiting (7).

$$r_{DADBS} = k_1 \, c_{DADBS} + k_2 \, c_{DADBS}^2$$

This polynomial model describes the measured data indeed very accurately, as seen in Fig.10A. The ad/desorption limitation (equation 11) of the SiO_2-MOCVD process was not observed; the reaction rate at such high concentrations could not be

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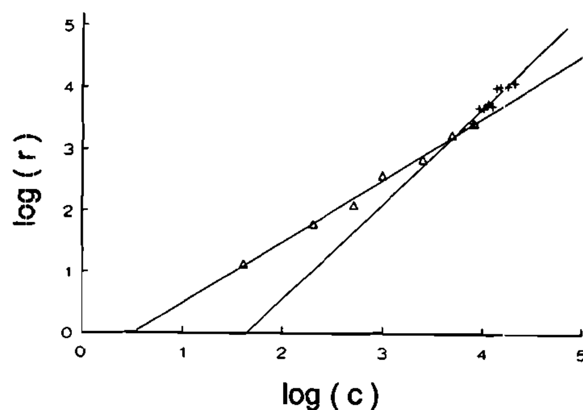

Figure 9. Order determination for the deposition rate of SiO_2 from DADBS by a double logarithmic plot of the reaction rate (r) versus the concentration (c).

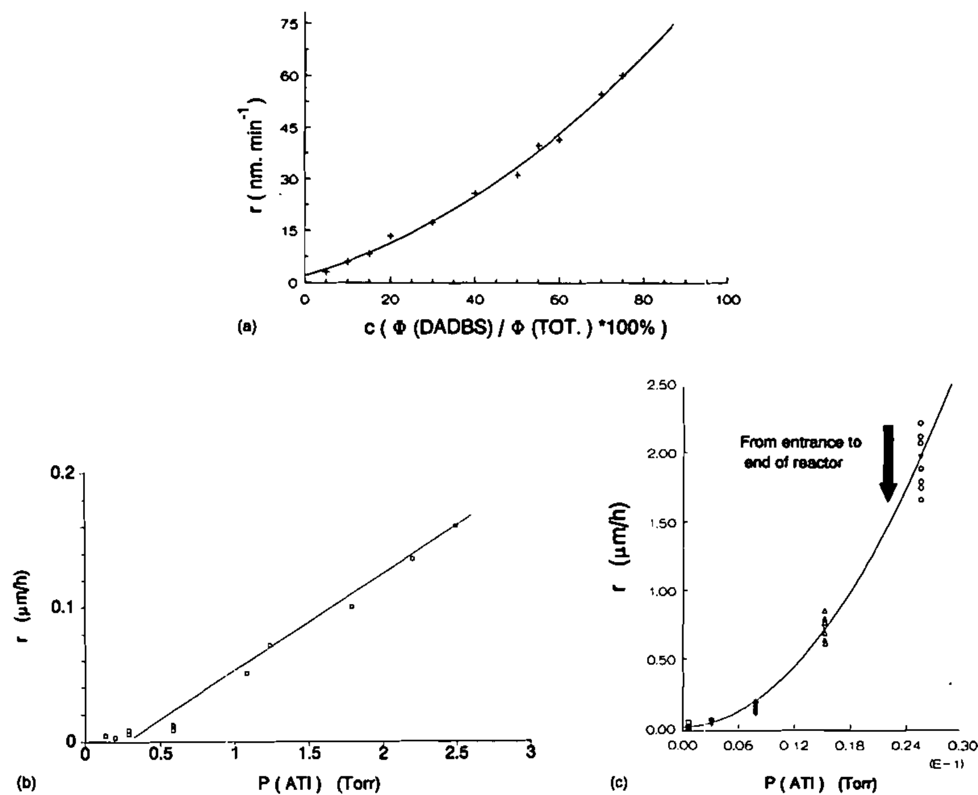

Figure 10. Measured and fitted reaction rates of SiO_2 deposition at atmospheric pressure (a), of Al_2O_3 at atmospheric (b) and at low pressure (3 torr) (c) as a function of the precursor concentration in the vapor.

determined due to spallation of the coatings within a few minutes, which leads to unacceptable errors in those data.

The deposition of ATI is a first order process at atmospheric pressure (Fig.10B) and a second order process at low pressure (3 torr) (Fig.10C). This can be explained when the dehydration reaction of AlOOH is rate limiting (8).

$$2\ O\text{-}Al\text{-}OH \rightarrow Al_2O_3 + H_2O \qquad (15)$$

This reaction explains the second order at low pressures, while the first eorder at atmospheric pressure can be explained by a combination of this reaction with the Langmuir adsorption model.

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The Reaction Rate as Function of the Position in the Furnace

In Fig.11 the reaction rate of the Al_2O_3-formation is given as a function of the position in the low pressure furnace. The reaction rate decreases from the inlet (position 0) to the outlet of the furnace (position 9). The decreasing reaction rate is explained by the fact that intermediate formation is fast compared with the consumption rate of intermediates. This is in agreement with the above mentioned model for the Al_2O_3 deposition.

The Decomposition Chemistry

The lack of thermodynamic data implies that products formed during MOCVD processes can not be predicted, and therefore the decomposition chemistry of metal organic compounds has to be monitored. Knowledge about the decomposition chemistry could lead to an improved precursor selection and a better layer quality by changing the reaction path.

Mass spectroscopic experiments as a function of the reaction temperature (Fig.12) indicate that decomposition of the MO-compounds involves three steps. In the first two steps, organic groups are formed and in the third step SiO_2 and Al_2O_3 are formed by polycondensation of the remaining acids. The products formed during decomposition of ATI are one propene and one 2-propanol (isopropanol) molecule in the first step and one propene group in the second step. In the first decomposition step of DADBS acetic acid anhydride is formed while in the second step 2-methyl propene is formed.

More theoretical work on the decomposition mechanism has been published elsewhere (7,8). The most important point of this mechanism is the formation of a rather stable 6-ring by bridging of the ß-hydrogen atom with an oxygen atom of another group of the same molecule (intra molecular reaction). Charge redistribution in this ring will be possible and the weakest bonds in this ring will be broken by releasing the mentioned organic groups.

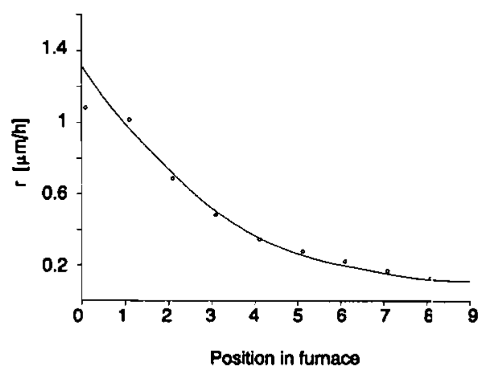

Figure 11. The deposition rate of Al_2O_3 at low pressure (3 torr) as a function of the position in the furnace (0 = entrance, 9 = outlet).

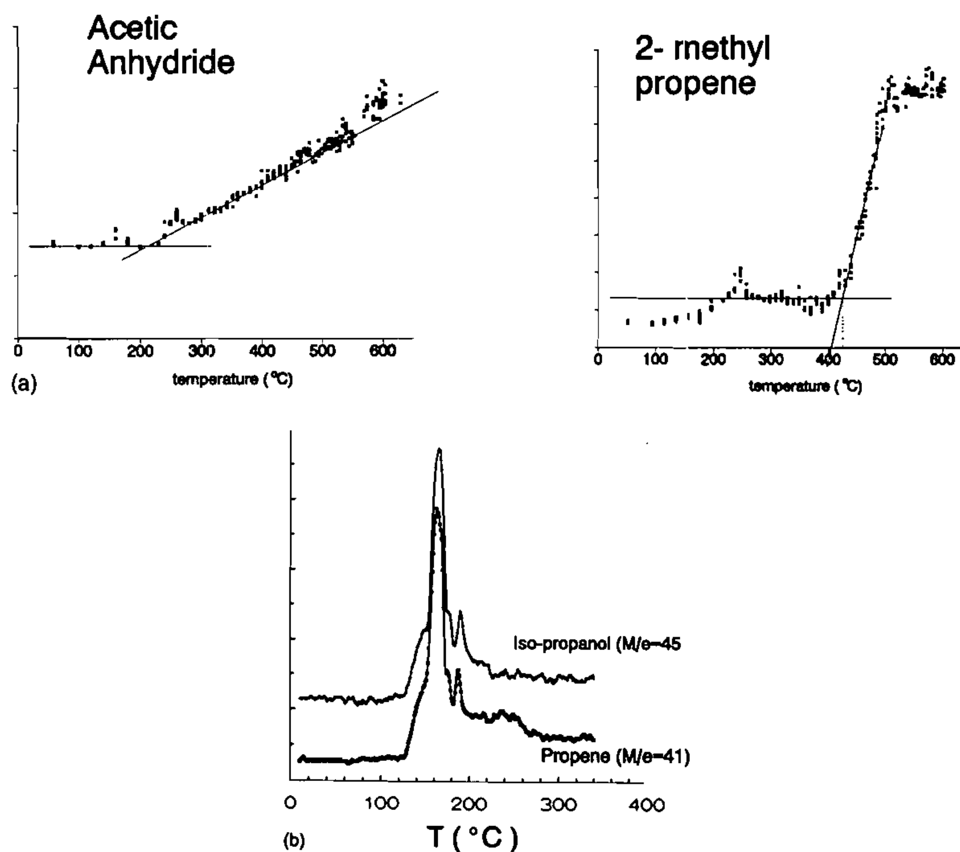

Figure 12. Vapor pressures of reaction products of the decomposition of DADBS (a) and ATI (b) measured by Mass Spectroscopy.

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CONCLUSIONS

Alumina and silica coatings have been deposited on Incoloy 800H by MOCVD. The influence of the reaction temperature and the partial pressure of the reactants have been studied. Both the decomposition of DADBS to SiO_2 and the decomposition of ATI to Al_2O_3 can be described by a model in which transport to and from the substrate and reactions on the substrate and in the gas phase take place. The deposition of SiO_2 is a combined first and second order reaction with an activation energy of 150 $kJ.mole^{-1}$. This is explained by two parallel, one second and one first order, gas phase reactions. The deposition of Al_2O_3 is a first order reaction at atmospheric pressures while at low pressure (3 torr) it is a second order. Both reactions have an activation energy of 30 $kJ.mole^{-1}$. This can be explained by a combination of a second order AlOOH dehydration reaction and a Langmuir adsorption model. The decomposition reaction of both DADBS and ATI involve a ß-hydrogen elimination reaction. DADBS decomposes to acetic acid anhydride, 2-methyl propene, SiO_2 and H_2O, while ATI decomposes to 2-propanol, propene, Al_2O_3 and H_2O.

LIST OF SYMBOLS

b	adsorption coefficient (atm^{-1})		
c	concentration ($mole.m^{-3}$)		
C	normalized concentration (-)		
D	diffusion constant ($m^2.s^{-1}$)		
J	molar flux ($mole.s^{-1}$)		
k	reaction rate constant	(first order reaction)	(s^{-1})
		(second order reaction)	($m^3.mole^{-1}.s^{-1}$)
l	length of reactor tube (m)		
P(i)	partial pressure of compound i (torr)		
r	reaction rate ($mole.m^{-3}.s^{-1}$)		
Sh	Sherwood number (-)		
x	normalized length (m)		
δ	thickness of stagnant boundary layer (m)		
Φ	volume flux ($m^3.s^{-1}$)		
Θ	surface coverage (-)		

INDICES

ads	adsorption
B.L.	boundary layer
des	desorption
gas	gas phase
I	intermediate in the gas phase
I^*	intermediate on the surface
m	reaction order constant

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n reaction order constant
P product
R reactant
s surface

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