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Kinetics of deposition of zirconia-based ceramics from $ZrCl_4$–H_2–CO_2–Ar gas mixtures

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Abstract

The kinetics of deposition of zirconia from the overall reaction: $ZrCl_4(g)+2H_2(g)+2CO_2(g) \rightarrow ZrO_2(s)+2CO(g)+4HCl(g)$ was studied from an experimental standpoint. A specially designed chemical vapor deposition reactor, equipped with a microbalance and accurate devices for controlling the experimental parameters (and especially the gas phase composition), was used to measure reliable growth rates of the ZrO_2 films over wide ranges of temperature, pressure, total flow rate and gas phase composition. The influence of the partial pressures of $ZrCl_4$, H_2, CO_2, Cl_2, HCl and argon was quantitatively investigated and the data used to derive kinetic laws. Finally, a tentative model of the chemical deposition process is proposed. It assumes three steps: (i) chemisorption of CO_2 on the substrate, (ii) reaction of adsorbed CO_2 with H_2 molecules resulting in H_2O adsorbed species and (iii) reaction of one $ZrCl_4$ molecule with two H_2O adsorbed species yielding zirconia and HCl, the third step being considered as the rate limiting step.

1. Introduction

The outstanding properties of zirconia, such as its high melting point, high chemical stability, good thermal insulating characteristics, have led in the past to a wide range of applications in the field of monolithic ceramics. More recently, new processing techniques such as chemical vapor deposition (CVD) or chemical vapor infiltration (CVI) gave rise to applications in other advanced fields: coating of cutting tools, elaboration of microelectronic devices [1] and densification of porous fiber preforms with a view to prepare ceramic matrix composites (CMCs) [2].

Many different chemical systems have been considered for the CVD of ZrO_2, the main difference between them lying in the nature of the gaseous species which carries the zirconium element. Previous researchers have used organometallic compounds such as alkoxides [3, 4]; $Zr(acac)_4$, $Zr(tfacac)_4$, $Zr(thd)_4$, $Zr(hfacac)_4$ [5–7] (where acac is acetylacetonate, tfacac is trifluoroacetylacetonate, thd is tetramethylheptadionate and hfacac is hexafluoroacetylacetonate) or zirconium halides and especially $ZrCl_4$ [1, 2, 8] or even $ZrOCl_2$ [9]. In all cases, the oxygen source species was either water, molecular oxygen or H_2–CO_2 mixtures.

Besides all these studies, whose aim was mainly to establish the feasibility of the CVD of zirconia from given precursors, very few studies tried to go

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further in order to work out the deposition mechanism. However, such a goal is of major interest in some advanced processing techniques. As an example, knowledge of the kinetic laws is a prerequisite for the calculation of the thickness profile of a zirconia deposit along a pore with a view to model the densification of a porous body (*e.g.* a fiber preform) in the processing of ZrO_2 matrix composites according to the isothermal/isobaric CVI technique [10–12]. Wahl *et al.* gave an overall activation energy for the deposition of ZrO_2 from $ZrCl_4$–O_2–Ar [8]. Minet *et al.* described the influence of the main parameters (temperature T, total pressure P and total gas flow rate Q) on the deposition of ZrO_2 from $ZrCl_4$–H_2–CO_2–Ar [13]. In a related field, some studies were devoted to the CVD of other refractory oxides such as TiO_2 [14] and alumina [15–17].

The aim of the present contribution, which deals with the CVD of ZrO_2 from $ZrCl_4$–H_2–CO_2–Ar, is to show quantitatively the dependence of the ZrO_2 growth rate on the experimental CVD parameters (*i.e.* T, P, Q and initial gas phase composition) and to derive the kinetic laws for the experimental conditions under which the kinetics of zirconia deposition is controlled by the heterogeneous surface reactions. Finally, a first approach to the chemical mechanisms involved in the deposition process of ZrO_2 will be tentatively proposed.

2. Experimental details

The CVD of zirconia from a $ZrCl_4$–H_2–CO_2–Ar gas mixture is based on the hydrolysis of gaseous $ZrCl_4$ by water resulting from the hydrogen reduction of CO_2 at high temperatures. It proceeds according to the generally accepted overall mechanisms:

$$2H_2(g) + 2CO_2(g) \rightleftharpoons 2H_2O(g) + 2CO(g) \qquad (1)$$

$$ZrCl_4(g) + 2H_2O(g) \rightleftharpoons ZrO_2(s) + 4HCl(g) \qquad (2)$$

or by combining (1) and (2):

$$ZrCl_4(g) + 2CO_2(g) + 2H_2(g) \longrightarrow ZrO_2(s) + 2CO(g) + 4HCl(g) \qquad (3)$$

with $\Delta G^{0,R}_{1200} = -189.85$ kJ mol^{-1}. It has been shown by Minet *et al.* that when equilibrium is reached, $ZrCl_4$ is quantitatively reacted into ZrO_2 as long as the initial gas mixture contains enough hydrogen and carbon dioxide to form the required amount of water [18]. Since reaction (1) is rather slow, even at temperatures as high as 1300 K, kinetics play an important role in the CVD of zirconia and the H_2–CO_2 gas mixture can be considered as a reservoir of water.

The zirconia films were obtained with an instrumented CVD apparatus schematically shown in Fig. 1. Gaseous $ZrCl_4$ is formed in line by reacting chlorine with an excess of zirconium chips set in a graphite crucible at about 623 K. An approach of the formation of $ZrCl_4$ and of zirconium subchloride by-products has been presented in detail elsewhere [19]. The $ZrCl_4$ vapor

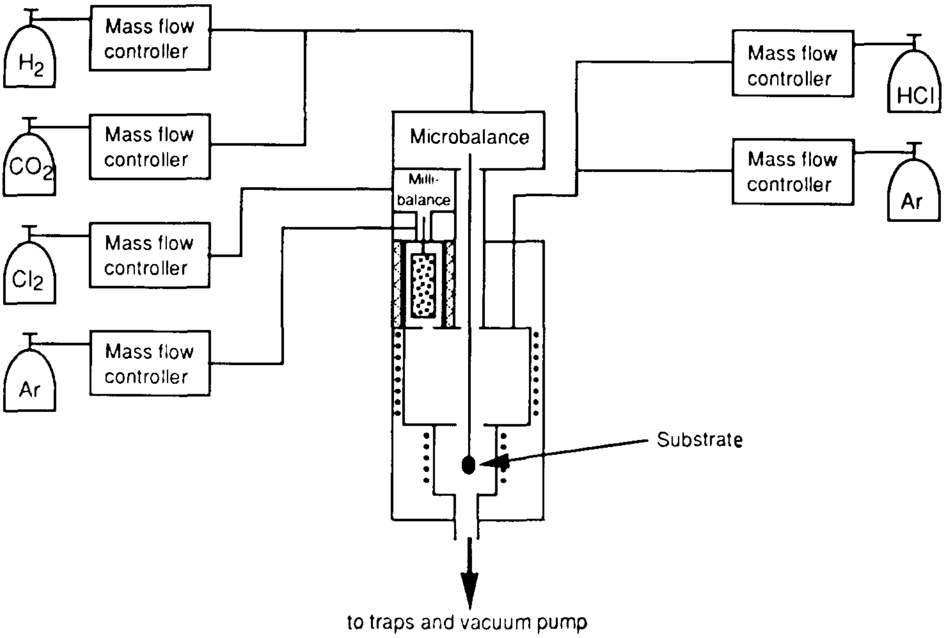


Fig. 1. Apparatus used for the CVD of ZrO_2 (schematic).

flow is then admitted in a preheating and mixing stage. H_2 and CO_2 are mixed together at room temperature, the mixture is preheated and finally admitted in the center of the CVD chamber. The $ZrCl_4$–Ar gas flow is mixed with the H_2–CO_2 gas flow just above the substrate to be coated, in order to avoid an early hydrolysis of $ZrCl_4$.

The CVD reactor itself consists of a vertical graphite tube (60 mm in diameter, 350 mm in length) heated with a r.f. coil set outside. The chlorinator is a superalloy cylinder capped with two flanges and heated with an electrical resistance. The whole assembly is set inside a water-cooled stainless steel protective chamber swept with a flow of argon in order to prevent any leak of reactants from the CVD graphite tube into the protective chamber.

The temperatures of the CVD zone and zirconium chlorinator are controlled by thermocouples. All the gas flow rates are measured with accurate mass flowmeters (ASM AFC 25), except that of $ZrCl_4$ which is calculated in line from a recording with a millibalance (Mettler PM400) of the weight loss of the crucible containing the zirconium chips bead *vs.* time. The total pressure is controlled with a pressure regulation device (MKS 252A).

The experiments were performed with chlorinator temperature between 623 and 923 K and deposition temperature ranging from 1473 to 1873 K. A quasi-isothermal zone ($\Delta T = \pm 6$ °C) was observed over at least 50 mm in the vertical graphite tube. The substrate consisted of a cylindrical sample of alumina (10 mm in diameter; 1 mm thickness) hung on a microbalance (Setaram B85) with a tungsten filament. The mass of zirconia deposited on the substrate could therefore be continuously recorded versus time with an accuracy of 2.5 μg.

3. Results

3.1. *Influence of the main CVD parameters on the deposition rate of zirconia*

3.1.1. *Temperature*

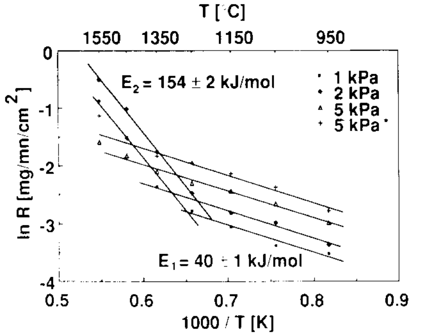
The thermal variations of the deposition rate of zirconia, presented as Arrhenius plots, are shown in Fig. 2, for various conditions of total pressure and argon flow rate. Within the temperature range studied, the thermal variations of the ZrO_2 deposition rate obey different laws depending on the value of the total pressure. At low total pressures ($P=1$ or 2 kPa), the thermal variations of the growth rate obey Arrhenius laws with an apparent activation energy of $E_1=40$ kJ mol^{-1} for $1223\ K<T<1523\ K$ and of $E_2=154$ kJ mol^{-1} for $1523\ K<T<1823\ K$. At a higher total pressure ($P=5$ kPa), the transition between the two Arrhenius laws is no longer observed (or it has been shifted to higher temperatures) and the data obey a single Arrhenius law with an apparent activation energy of $E_1=40$ kJ mol^{-1}. Furthermore, it seems that the effect of a dilution of the reactants with an inert gas (*i.e.* argon) is simply to change the deposition rate without changing the apparent activation energy. Finally, no transition between a mass transfer controlled regime to a regime kinetically controlled by the heterogeneous surface reactions is observed.

3.1.2. *Total flow rate (Q_t)*

The variations of the deposition rate of zirconia as a function of the total flow rate Q_t are shown in Fig. 3 for $T=1323$ and 1623 K. The influence of Q_t on the deposition rate depends on the reactor geometry; however, it is of prime importance for the assessment of the kinetics rate controlling factor in the CVD process. For both temperatures, raising Q_t increases the deposition rate of zirconia. Since the experiments were performed at constant total pressure and gas phase composition, the variations of the deposition rate can be assigned to hydrodynamic effects rather than to chemical reaction effects. In the following, flow rates are in cm^3 min^{-1} measured under standard *TP* conditions (*i.e.* sccm).

3.1.3. *Total pressure*

The last CVD parameter which could induce a transition between a kinetic process rate controlled by mass transfer and a kinetic process rate controlled by heterogeneous surface reactions, is the total pressure *P*. Thus, the variations of *R* as a function of *P* were studied and the data are shown in Fig. 4 for two values of Q_t. For $Q_t=534$ cm^3 min^{-1}, the variations of *R* as a function of *P* undergo a minimum at $P=2$ kPa and a rather sharp maximum at $P=6$ kPa. When Q_t is raised from 534 to 1114 cm^3 min^{-1} (by



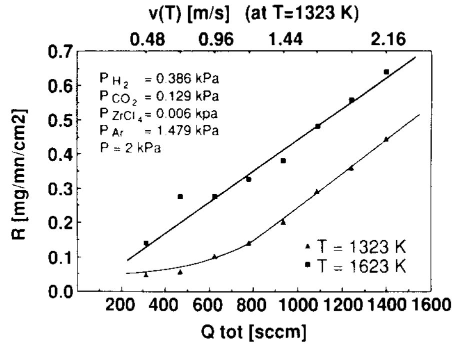


Fig. 2. Arrhenius plots of the thermal variations of the zirconia deposition rate for the various pressures, $Q_{H_2}=60$ cm^3 min^{-1}, $Q_{CO_2}=20$ cm^3 min^{-1}, $Q_{ZrCl_4}=3.7$ cm^3 min^{-1}, $Q_{Ar}=230$ cm^3 min^{-1}, $Q_{Ar*}=790$ cm^3 min^{-1}.

Fig. 3. Variations of the zirconia deposition rate as a function of the total gas flow rate at $T=1323$ K and 1623 K (the axial linear gas velocities $v=dz/dt$ have been calculated from Q_{tot} for $T=1323$ K).

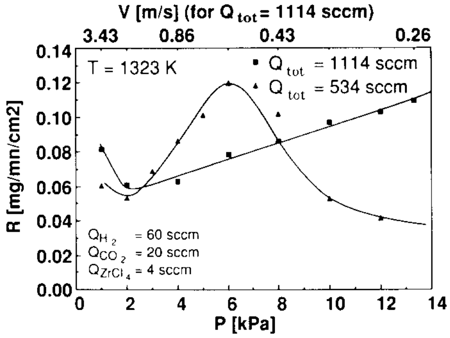


Fig. 4. Variations of the zirconia deposition rate as a function of the total pressure (the axial linear gas velocities $v=dz/dt$ have been calculated from $Q_{tot}=1114$ cm^3 min^{-1}).

adding argon), this maximum (if it still occurs) is shifted towards higher pressure values (with the result that no further decrease in growth rate is observed at high P). However, the minimum in R at $P=2$ kPa is still present.

3.2. Influence of the partial pressures and assessment of the apparent reaction orders

When the chemical reactions are the rate-controlling step in the kinetic processes, it is of interest to assess experimentally apparent reaction orders with respect to the various species introduced in the gas phase, with a view to derive a complete kinetic law and to suggest a chemical mechanism for the deposition process. Thus, the influence of the partial pressures of $ZrCl_4$, H_2, CO_2, Cl_2, HCl and argon on the deposition rate of zirconia R was quantitatively studied at $T=1323$ and 1623 K. For a species i, the experiments were performed by maintaining constant flow rates Q_j and the partial pressures

P_j of all the species j (with $j \neq i$) and by varying the total pressure and the partial pressure P_i of the species i under consideration. The data are shown in Figs. 5–10 as $\ln R = f(\ln P_i)$ curves. These curves are expected to be straight lines whose slopes are the apparent reaction orders, in agreement with a kinetic law of the following kind:

$$R = k_T(P_{ZrCl_4})^{n_1}(P_{H_2})^{n_2}(P_{CO_2})^{n_3}(P_{Cl_2})^{n_4}(P_{HCl})^{n_5}(P_{Ar})^{n_6} \tag{4}$$

where k_T is the kinetics constant at temperature T and n_i (with $i = 1, 2, 3 \ldots 6$) the apparent reaction orders for species i.

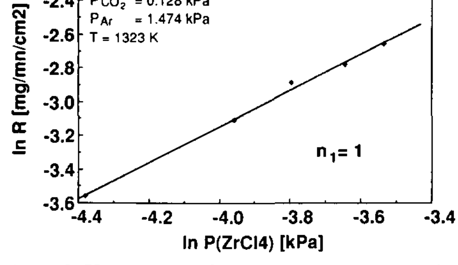
3.2.1. Apparent reaction orders at T=1323 K

The plot $\ln R = f(\ln P_i)$ with $i = ZrCl_4$, shown in Fig. 5, exhibits an apparent reaction order $n_1 = 1$. It should be emphasized that although both the total pressure P and the total gas flow rate were varied, these variations were maintained within narrow ranges (2.000 kPa $< P <$ 2.016 kPa and 312 cm^3 min^{-1} $< Q_t <$ 314.6 cm^3 min^{-1}).

The plots $\ln R = f(P_{H_2})$ drawn from the data recorded during two different runs, are shown in Fig. 6 (with 2.000 kPa $< P <$ 2.321 kPa and 312 cm^3 min^{-1} $< Q_t <$ 362 cm^3 min^{-1}). They are straight lines with the same slope yielding an apparent reaction order of $n_2 = 2$.

Finally, the plots $\ln R = f(P_{CO_2})$ drawn from the data derived from two different runs, are shown in Fig. 7 (with 2.000 kPa $< P <$ 2.641 kPa and 312 cm^3 min^{-1} $< Q_t <$ 362 cm^3 min^{-1}). Both plots are straight lines with the same slope corresponding to an apparent reaction order of $n_3 = 0.5$.

From eqn. (3) it appears that $ZrCl_4$, H_2 and CO_2 are the only reactants which should be present in the initial feed gas of the CVD apparatus. However, it could be of some interest to investigate whether or not chlorine (which is used to generate $ZrCl_4$ and may not be totally consumed), HCl (the main reaction product) and argon (used as a diluent gas) have an influence on the deposition rate of zirconia. Thus, experiments were performed in which the partial pressures of Cl_2, HCl and argon were successively varied. The data are shown in Figs. 8–10.



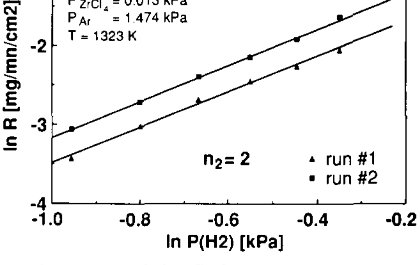
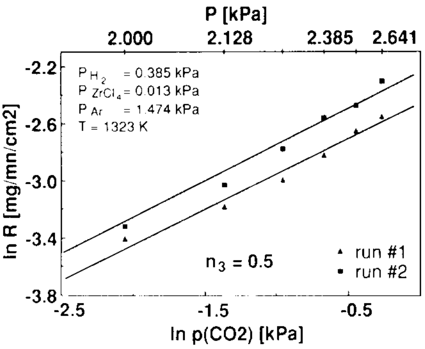


Fig. 5. Variations of the deposition rate of zirconia as a function of the $ZrCl_4$ partial pressure.

Fig. 6. Variations of the deposition rate of zirconia as a function of the H_2 partial pressure.



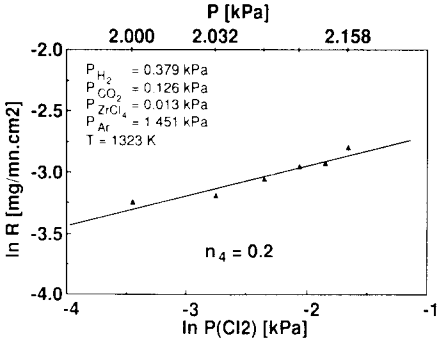
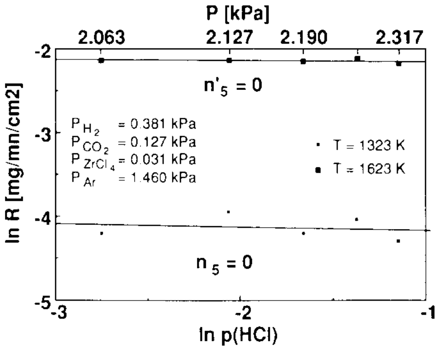


Fig. 7. Variations of the deposition rate of zirconia as a function of the CO_2 partial pressure.

Fig. 8. Variations of the deposition rate of zirconia as a function of the Cl_2 partial pressure.



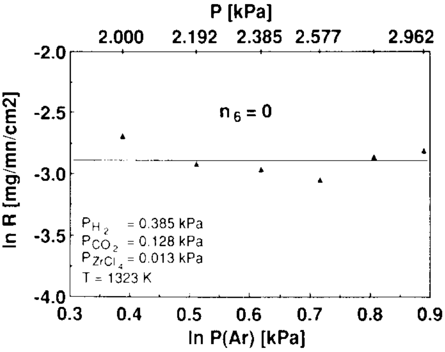


Fig. 9. Variations of the deposition rate of zirconia as a function of the HCl partial pressure.

Fig. 10. Variations of the deposition rate of zirconia as a function of the argon partial pressure.

As could be expected, the apparent reaction order with respect to argon derived from the data of one single run (with 2.000 kPa$<P<$2.962 kPa and 312 cm^3 min^{-1}$<Q_t<$462 cm^3 min^{-1}) was observed to be zero ($n_6=0$) (Fig. 10). In a similar manner, the apparent reaction orders with respect to Cl_2 and HCl were observed to be $n_4=0.2$ and $n_5=0.04$ and were considered to be zero, at least in a first approximation (Figs. 8 and 9).

From the data reported above, the following kinetic law is proposed for $T=1323$ K and P close to 2 kPa:

$$R=k_0 \exp\left(-\frac{E_a}{RT}\right) P_{ZrCl_4} P_{CO_2}^{1/2} P_{H_2}^{2}$$

where $E_a=40\pm1$ kJ mol^{-1}, $k_0=6\times10^{-8}$ mg mn^{-1} cm^{-2} Pa$^{-3.5}$ and R is the perfect gas constant.

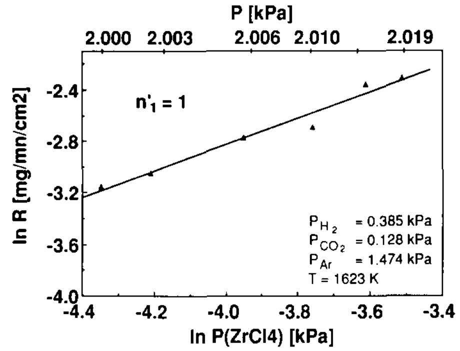
3.2.2. *Apparent reaction orders at T=1623 K*

The Arrhenius plots shown in Fig. 2 suggest that a different chemical mechanism may occur at high temperatures. A new series of experiments was therefore performed at $T = 1623$ K in order to establish whether or not the apparent reaction orders would be equal to those derived from the experiments run at $T = 1323$ K.

From the graphs $\ln R = f(P_i)$ shown in Figs. 11–14, it appears that the apparent reaction orders with respect to $ZrCl_4$ and CO_2 are unchanged ($n'_1 = 1$ and $n'_3 = 0.5$ respectively). In a similar manner, those related to Cl_2 and HCl were observed to be still equal to zero ($n'_4 = n'_5 \approx 0$) whereas that corresponding to argon was not determined and was also assumed to be zero.

However, the influence of the partial pressure of hydrogen on the deposition rate of zirconia, as shown in Fig. 12, appears to be unexpectedly complex. In a first approximation, the data recorded from three different runs could be fitted with two apparent reaction orders $n'_2 = 2.3$ for $P_{H_2} < 0.5$ kPa and $n'_2 = 0.5$ for $P_{H_2} > 0.5$ kPa.

As a consequence, for $T = 1623$ K and P close to 2 kPa, the data have to be fitted with two different kinetic laws depending on the values of the



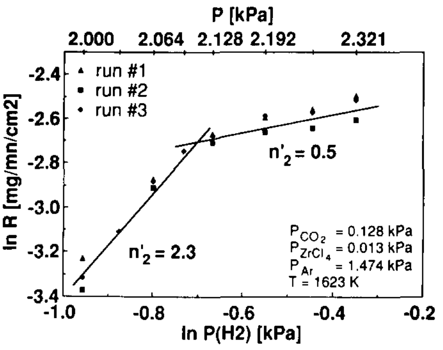
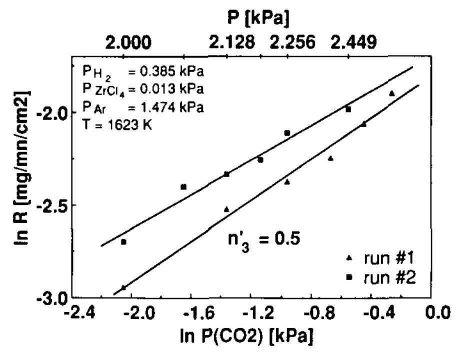


Fig. 11. Variations of the deposition rate of zirconia as a function of the $ZrCl_4$ partial pressure.

Fig. 12. Variations of the deposition rate of zirconia as a function of the H_2 partial pressure.



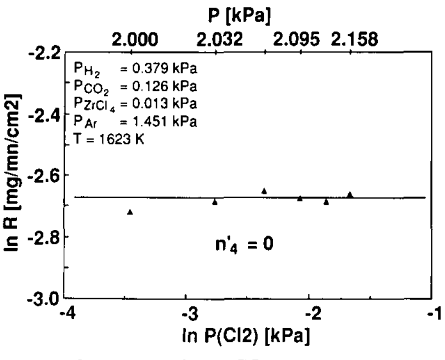


Fig. 13. Variations of the deposition rate of zirconia as a function of the CO_2 partial pressure.

Fig. 14. Variations of the deposition rate of zirconia as a function of the chlorine partial pressure.

hydrogen partial pressures:

$$R = k_0 \exp\left(-\frac{E_a}{RT}\right) P_{ZrCl_4} P_{CO_2}^{1/2} P_{H_2}^{2.3}$$

with $E_a = 154 \pm 2$ kJ mol^{-1} and $k_0 = 4.1 \times 10^{-5}$ mg mn^{-1} cm^{-2} $Pa^{-3.8}$ for $P_{H_2} < 0.5$ kPa and:

$$R = k_0 \exp\left(-\frac{E_a}{RT}\right) P_{ZrCl_4} P_{CO_2}^{1/2} P_{H_2}^{1/2}$$

with $E_a = 154 \pm 2$ kJ mol^{-1} and $k_0 = 3.1$ mg mn^{-1} cm^{-2} Pa^{-2} for 0.5 kPa $< P_{H_2} < 0.705$ kPa.

4. Discussion

Water formation is a step which has to be taken into account in the chemical mechanism of zirconia deposition from the $ZrCl_4$–H_2–CO_2 system. The kinetics of this reaction were experimentally studied by Tingey, who derived, over the temperature range 1073–1323 K, a high activation energy of 326 kJ mol^{-1}, a homogeneous mechanism being involved, even in the presence of a graphite surface [20]. However, this reaction of water–gas conversion was found to be catalyzed by various oxide solid surfaces such as alumina, as shown by Amenomiya who reported an activation energy as low as 67 kJ mol^{-1} [21]. The kinetic study of alumina deposition on alumina substrate in the $AlCl_3$–H_2–CO_2 system, performed by Colmet *et al.*, evidenced an activation energy ranging from 60 to 120 kJ mol^{-1} for temperatures between 1173 and 1473 K [16]. Lastly, Minet *et al.*, in their experimental approach of the CVD of zirconia from ZrO_2–H_2–CO_2 gas mixtures, found an activation energy of the kinetic process close to 400 kJ mol^{-1} in the temperature range 1173–1273 K where the deposit consisted mainly of monoclinic zirconia [13].

The temperatures investigated in the present study being higher than 1273 K, zirconia is probably mainly deposited as tetragonal phase. The relatively low activation energies (40 and 154 kJ mol^{-1}) are found to be rather close to that obtained by Amenomiya. This result could be explained by a catalytic effect of zirconia on which H_2 and CO_2 gaseous species are heterogeneously converted into water vapor. The thermal activation, observed over a wide temperature range, could suggest a control of the kinetic process by the chemical reactions occurring at the growing surface. This result is in contrast with the rise of the experimental deposition rate as a function of the total flow rate, which is rather typical for a mass transfer control (Fig. 3). Such a kinetic process with an increase of the growth rate versus both temperature and total flow rate could be interpreted on the basis of two simultaneous competing mechanisms resulting in zirconia deposition, the first one governed by chemical reactions and the second one by mass transfers. In this case, the mechanism with the highest rate gives its rate to the overall process. In the low temperature range (*e.g.* $1273\ \mathrm{K} \leqslant T \leqslant 1523\ \mathrm{K}$ for $P = 2$ kPa and $Q = 300\ \mathrm{cm^3\ min^{-1}}$), the very low activation energy can be attributed either to the convection and/or diffusion step for gaseous species such as H_2, CO_2, H_2O or to a highly favored heterogeneous reaction (*e.g.* the water formation catalyzed by the surface or zirconia synthesis from adsorbed H_2O species). For higher temperatures, the Arrhenius plots exhibit a change towards a higher activation energy, which could mean that the thermal energy is high enough to promote the homogeneous reaction of water formation, giving rise to another deposition mechanism with H_2O vapor species. The influence of the total pressure on the deposition rate, measured at 1323 K, is typical behavior for a kinetic process controlled by chemical reactions, as already reported in the CVD of zirconia or alumina [13].

In the case of a catalytic effect of zirconia surface on the chemical process, a heterogeneous mechanism can be tentatively proposed for the deposition of zirconia from $ZrCl_4$–H_2–CO_2. Among the species diffusing towards the surface, the unsaturated molecule CO_2 is assumed to be preferentially chemisorbed. Some of these adsorbed molecules can react with hydrogen giving rise to adsorbed H_2O molecules, resulting after reaction with $ZrCl_4$ in solid zirconia and HCl molecules, according to the following set of elementary equations:

$$CO_2 + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO_2^* \tag{5}$$

$$CO_2^* + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2O^* + CO \tag{6}$$

$$2H_2O^* + ZrCl_4 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ZrO_2(s) + 4HCl + 2* \tag{7}$$

where $*$ stands for a site of adsorption and i^* for an adsorbed species.

Among these reactions, the formation of zirconia according to eqn. (7) which involves the occurrence of two H_2O molecules adjacently adsorbed, is probably the limiting step of the process. As a consequence, the equilibria (5) and (6) can be considered to occur, the corresponding constants being written as:

$$K_1 = \frac{k_1}{k_{-1}} = \frac{\theta_{CO_2}}{\theta P_{CO_2}} \tag{8}$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{\theta_{H_2O} P_{CO}}{\theta_{CO_2} P_{H_2}} \tag{9}$$

where θ is the relative amount of free surface sites and θ_i the equilibrium coverage of species i which can be calculated on the basis of the Langmuir model as a function of constant K_i and partial pressure P_i. θ is given by:

$$\theta = 1 - \theta_{CO_2} - \theta_{H_2O} \tag{10}$$

which gives, by using eqns. (8) and (9):

$$\theta = \frac{1}{1 + K_1 P_{CO_2} + K_1 K_2 P_{H_2} P_{CO_2} P_{CO}^{-1}} \tag{11}$$

By taking into account the probable dominant coverage of CO_2 species, the amount of free sites can be reduced to:

$$\theta = \frac{1}{K_1 P_{CO_2}} \tag{12}$$

However, the deposition rate of zirconia is given by the rate of step (7) which can be expressed as:

$$R = k_3\, \theta_{H_2O}^2 P_{ZrCl_4} - k_{-3}\, \theta^2 P_{HCl}^4 \tag{13}$$

which becomes, by using eqns. (8) and (9):

$$R = k_3 K_1^2 K_2^2\, \theta^2 P_{H_2}^2 P_{CO_2}^2 P_{CO}^{-2} P_{ZrCl_4} - k_{-3}\, \theta^2 P_{HCl}^4 \tag{14}$$

and finally, with eqn. (12):

$$R = k_3 K_2^2 P_{ZrCl_4} P_{H_2}^2 P_{CO}^{-2} - k_{-3} K_1^{-2} P_{HCl}^4 P_{CO_2}^{-2} \tag{15}$$

The second term of this theoretically derived kinetic law, which quantifies the etching rate in the chemical process, is probably relatively low (*e.g.* because of a high value of K_1 and a low value of k_{-3}). The orders 1 with respect to $ZrCl_4$ and 2 with respect to H_2 are in good accordance with the corresponding experimental orders. The order with respect to CO_2, experimentally found to be ½, could correspond to the dependence in $P_{CO_2}^{-2}$ occurring in the etching term of the kinetic law. The only disagreement concerns the reaction order with respect to HCl (which should not be zero if the kinetic law is totally valid). Finally, an investigation of the influence of CO species and more experiments with HCl would allow the validity of the proposed kinetic law to be confirmed.

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