Corrosion resistant coatings (Al_2O_3) produced by metal organic chemical vapour deposition using aluminium–tri-*sec*-butoxide

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Abstract

The metal organic chemical vapour deposition (MOCVD) of amorphous alumina films on steel was performed in nitrogen at atmospheric pressure. This MOCVD process is based on the thermal decomposition of aluminium–tri-*sec*-butoxide (ATSB). The effect of the deposition temperature (within the range 290–420 °C), the precursor vapour pressure (5.33×10^{-3} – 2.67×10^{-2} kPa), and the gas flow (6.5 – 12.5 l min $^{-1}$) of the MOCVD process have been studied in relation to corrosion properties at high temperatures. The corrosion experiments were performed at 450 °C in a gas atmosphere containing 1% H_2S , 1% H_2O , 19% H_2 , and balanced Ar.

It was found that the amount of corrosion products on an alumina film (0.20 ± 0.05 mg cm $^{-2}$)–AISI 304 combination decreased with increasing deposition temperature of the coating. This was more pronounced for the products formed through the coating owing to a certain porosity. The crack density, where products were also formed, was almost unaffected.

1. Introduction

For the deposition of alumina several reactants have been investigated [1–11], for example AlCl_3 which can react with carbon dioxide and hydrogen under the formation of aluminium oxide. These layers are mostly used in the electronic industry for the fabrication of metal oxide semiconductor–field-effect transistors [12–14]. The process has to be carried out at high temperatures, normally between 850 and 1600 °C, which demands a high energy consumption. Furthermore, the experimental procedure needs several gas streams, leading to an increased amount of parameters influencing the properties of the alumina films. For example, owing to different deposition temperatures, several well-defined oxide films can be obtained with a desired structure. At temperatures of about 850 °C an amorphous layer [12] can be obtained, as can a fine grained polycrystalline structure [13] at temperatures up to 1000 °C, an alpha phase at temperatures up to 1400 °C, and at higher temperatures a single crystal structure [14] can be obtained.

The deposition by means of compounds such as AlCl_3 , is called chemical vapour deposition (CVD). It is also known that metal alkoxides are sometimes excellent precursors for the deposition of metal oxides such as SiO_2 , TiO_2 , Cr_2O_3 and Al_2O_3 [15–18]. The use of

these precursors offers several attractions: the metal alkoxides can be purified to a high degree, they contain more than enough oxygen for the formation of the desired oxide, and, last but not least, the much lower deposition temperature compared with normal CVD can also be very attractive if the substrate does not suffer under high temperatures. The deposition of thin oxide films by thermal decomposition of organometallic compounds is normally called metal organic chemical vapour deposition (MOCVD). The trivalent metal alkoxides with no alkyl groups are frequently considered to be relatively stable at elevated temperatures. They can be heated without decomposition. Thus for our experiments only metal (aluminium) alkoxides are relevant such as Al–tri-*tert*-butoxide (ATTB), Al–tri-*sec*-butoxide (ATSB), Al–tri-*n*-butoxide (ATNB), Al–tri-isopropoxide (ATI), and Al–acetyl-acetonate (AAA).

The use of ATSB was reported only by Okuyama *et al.* [19] and Kodas *et al.* [20] for the production of ultrafine aluminium oxide aerosol particles by thermal decomposition of ATSB. Physical properties of ATSB and some other aluminium alkoxides were reported by Sladek [2] and Wilhoit [21] regarding the equilibrium partial pressure.

From the literature it is clear that until today nothing has been reported about MOCVD using ATSB as the metal alkoxide for the formation of an adherent and dense alumina film.

The aim of our study was the development and testing of dense and adherent thin alumina films, ap-

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plied on metallic materials. These ceramic coatings should protect the underlying substrate against the corrosive environments at high temperatures such as coal gasification and gas turbine atmospheres. In this paper the results are presented regarding the deposition of alumina by MOCVD from ATSB. The kinetic aspects in relation to the protectiveness of the coating in simulated coal gasification atmospheres are discussed.

2. Experimental details

Depositions were performed on AISI 304 (18% Cr, 8% Ni, 0.08% C, 1% Si, 2% Mn, 71% Fe). The AISI 304 samples were cut from an electropolished sheet and subsequently ultrasonically cleaned for 30 min in RBS soap, hexane and ethanol. Finally, the samples were immersed in Struer's etching fluid (5% solution of 3 M nitric acid in ethanol) for 15 min, washed with pure ethanol and dried in air at room temperature. For the corrosion experiments, the samples were coated with $0.20 \pm 0.05 \text{ mg cm}^{-2}$ alumina.

Alumina films were produced by decomposing Al-*tri-sec-butoxide* (ATSB, Janssen Chimica) under atmospheric circumstances. A schematic view of the experimental apparatus is given in Fig. 1. A stream of pure nitrogen gas was passed through a coil in a silicon oil bath at 138°C where the nitrogen gas was saturated with the ATSB. The resulting gas was mixed with another nitrogen gas stream to achieve the required concentration of the precursor before entering the reaction tube. The sample was attached to a ceramic tube with a thermocouple on the inside for accurate measurement of the sample temperatures. The standard conditions for the MOCVD process were also used for Figs. 5–12, and exceptions are mentioned in the figure captions: silicon oil bath with ATSB, 138°C ; carrier gas flow (N_2), 1300 ml min^{-1} (STP); diluent gas flow (N_2), 5200 ml min^{-1} (STP); substrate temperature, 330°C .

The corrosion experiments were carried out for 24 h in a closed system. Before starting the experiment, the system was flushed with argon (saturated with water at 15°C) for 20 h with a flow rate of 7 l h^{-1} (STP). The mixture of gases (1% H_2S , 1% H_2O , 19% H_2 , bal. Ar.) was introduced afterwards, with a flow rate of 16 l h^{-1} . After 2 h the furnace was heated to the temperature at which the experiments were performed. The whole system was flushed for another 2 h and then closed. It was previously found that no relevant difference in corrosion rate and corrosion products was obtained between a closed system and a system with a continuous flow, if the reactive gas consumption did not exceed more than 18%.

The morphology and the composition of the layers were investigated by means of optical microscopy and

Atmospheric MOCVD

Fig. 1. Schematic view of the MOCVD apparatus: 1, thermocouple with specimen; 2, furnace; 3, nitrogen 5.0 carrier gas; 4, container with ATSB at constant temperature; 5, nitrogen dilution gas.

scanning electron microscopy (SEM) (JEOL M 35 CF) equipped with an EDX analysis system (Kevex Delta, class III). The deposition rate of the films on the metallic substrate was determined by weighing the samples before and after the deposition.

3. Results and discussion

3.1. Deposition experiments

The effect of the deposition temperature (290 – 420°C) on the rate ($\text{mg cm}^{-2} \text{ h}^{-1}$) is shown in Fig. 2. The overall activation energy for the heterogeneous reaction is $83 \pm 5 \text{ kJ mol}^{-1}$ (calculated for the reaction rate limited film growth). At higher temperatures the deposition rate increases more slowly than at lower temperatures. A further increase in temperature will result in a decreased deposition rate and becomes irreproducible with increasing temperature. This means that three regions can be distinguished: region 1, representing the deposition behaviour at low temperatures, shows a deposition rate controlled by reactions between the substrate and the precursor (reaction rate limited film growth); region 2, at higher temperatures, represents the deposition rate controlled by mass transport of the reactants in the gas phase (diffusion rate limited film growth); and region 3, at the highest temperatures, represents mass

Fig. 2. Deposition rate ($\text{mg cm}^{-2} \text{h}^{-1}$) of alumina as a function of the deposition temperature (K).

transport of the reactants as well as homogeneous gas-phase reactions.

The deposition rate ($\text{mg cm}^{-2} \text{h}^{-1}$) as a function of the partial pressure of ATSB (5.33×10^{-3} – 2.67×10^{-2} kPa) at various temperatures (330, 370, 400 and 420 °C) is given in Fig. 3. The reaction order of the deposition of alumina (from ATSB) could be calculated from the equation:

$$\ln[\text{deposition rate } (\text{mg cm}^{-2} \text{h}^{-1})] = k_1 + n \ln[\text{partial pressure ATSB (kPa)}] \quad (1)$$

where n is the reaction order and k_1 is a constant. It was found that in the temperature range 330–420 °C the deposition rate of alumina is about first order (1.0 ± 0.2) with respect to the initial concentration of ATSB. The overall reaction includes several steps, such as: (1) diffusion to and adsorption of the reactants on the substrate surface; (2) chemical reaction and diffusion on the surface; and (3) desorption and diffusion of products (gases) from the surface. In general one step predominates the overall reaction rate and, hence, represents the total resistance.

Fig. 3. Deposition rate ($\text{mg cm}^{-2} \text{h}^{-1}$) of alumina as a function of the concentration ATSB (kPa) and the deposition temperature (°C).

Fig. 4. Deposition rate ($\text{mg cm}^{-2} \text{h}^{-1}$) of alumina as a function of the gas flow (l min^{-1}) and the deposition temperature (°C).

In Fig. 4 the effect of the gas flow (l min^{-1}) on the deposition rate ($\text{mg cm}^{-2} \text{h}^{-1}$) is shown. At high temperatures the gas flow has a more pronounced effect on the deposition rate than at lower ones (< 370 °C), where the deposition rate was, within the accuracy of the experiments, practically independent of the gas flow.

A quantification of the MOCVD process can be performed by the 'film model', set up by Bird [23]. This model implies: (1) a stagnant boundary diffusion layer formed around the substrate with a thickness δ ; (2) reactions only taking place on the substrate surface; and (3) a first order process without homogeneous reactions taking place in the boundary layer. The deposition rate can now be described using the following simplified equation:

$$J = \frac{[\text{ATSB}]}{(1/k_r + 1/k_g)} \quad (2)$$

where D is the diffusion coefficient, J is the deposition rate, $[\text{ATSB}]$ is the concentration of ATSB, k_r is the rate constant of the surface reaction, $k_g = (D/\delta)$ is the mass transfer coefficient in the gas phase, and δ is the thickness of the diffusion boundary layer.

Two extreme situations can be observed: for $k_r/k_g \gg 1$ the deposition rate is determined by diffusion-limited growth, and for $k_r/k_g \ll 1$ the deposition rate is limited by the reaction rate. This equation implies that under reaction-rate-limited circumstances, the deposition rate is only a function of k_r , whereas it is only a function of k_g if the reaction is completely diffusion-controlled. This means that if limitation by diffusion takes place, the deposition rate is also a function of the total flow rate. At higher temperatures the deposition rate will increase proportional to the flow rate. This is in agreement with Fig. 4, where the deposition rate ($\text{mg cm}^{-2} \text{h}^{-1}$) is given as a function of the gas flow. Here it was found that at temperatures above 370 °C, the deposition rate increased by increasing the gas flow. From this figure it is also clear that the difference of the

deposition rates between 370 and 400 °C is much higher than between 400 and 420 °C. This can be explained by: (1) a change of the deposition regime from reaction limitation to diffusion limitation; and (2) a homogeneous reaction (alumina powder formation in the gas phase) which will become more pronounced at higher temperatures.

3.2. Corrosion experiments

In Figs. 5–7 the relative weight gain is shown, defined as $100\% \times$ (the ratio between the weight gain of a coated and an uncoated sample). From Fig. 5 it is clear that the amount of corrosion products (relative weight gain) tends to decrease with increasing deposition temperature. At deposition temperatures above 370 °C the relative weight gain scatters somewhat.

In Figs. 6 and 7 the relative weight gain is shown as a function of the initial precursor concentration and the gas flow. The deposition rate is directly related to the partial pressure of the precursor, as seen in Fig. 3. From these figures it is clear that the relative weight

Fig. 5. Bar diagram of the relative weight gain (%) of the specimens (after 24 h sulphidation at 450 °C) as a function of the deposition temperature (°C).

Fig. 6. Bar diagram of the relative weight gain (%) of the specimens (after 24 h of sulphidation at 450 °C) as a function of the vapour pressure of ATSB (kPa) and the deposition temperature (°C).

Fig. 7. Bar diagram of the relative weight gain (%) of the specimens (after 24 h of sulphidation at 450 °C) as a function of the gas flow (l min⁻¹) and the deposition temperature (°C).

gain is almost unaffected by changing the partial pressures of the precursor (concentration) between 5.33×10^{-3} and 2.67×10^{-2} kPa and a gas flow between 6.5 and 12.5 l min^{-1} .

In Figs. 8(a)–8(d) SEM pictures of the sulphidized samples are shown. These figures represent the surface of a sample coated under standard conditions and at deposition temperatures ranging from 330 °C to 420 °C. At higher deposition temperatures the corrosion attack decreases, especially by a reduced scale porosity. Especially, the FeS formation between the chain-like products is reduced. Cracks in the alumina films are responsible for the chain-like corrosion products, and are more pronounced near the edges.

Higher magnifications (Fig. 9) show that Fe sulphide is also formed through the alumina film, indicative of a porous structure of the film (deposition under standard conditions and after 24 h sulphidation). This is more pronounced at lower deposition temperatures.

Experiments were also performed by changing the ATSB concentration and gas flow. From the weight gain bar diagrams it is clear that the relative weight gain was not strongly affected by those variations. On the contrary, SEM observations show that at lower deposition temperatures the surface morphology of the corroded specimens has changed somewhat with respect to different ATSB concentrations. Depositions performed at low deposition rates result in a surface where corrosion products are mainly concentrated near the edges. At higher deposition rates corrosion products were found all over the specimens, and this was more pronounced at lower deposition temperatures than at higher ones. See Figs. 10 and 8(c) showing the surface morphology after sulphidation (deposition at 400 °C and a partial pressure of ATSB of 5.33×10^{-3} and 2.67×10^{-2} kPa, respectively).

The best protection of the alumina films against high temperature corrosion was obtained at high deposition

(a)

(b)

(c)

(d)

Fig. 8. SEM image of the surface morphology of coated samples after 24 h of sulphidation at 450 °C: (a) deposition temperature, 330 °C; (b) 370 °C; (c) 400 °C; and (d) 420 °C.

Fig. 9. SEM image of the surface morphology of a coated sample after 24 h of sulphidation at 450 °C showing Fe-rich sulphides products which were formed throughout the alumina scale.

temperatures both considering the relative weight gain of the specimens and the surface morphology after the corrosion experiments. Two types of corrosion products could still be found on the surface of the sulphidized specimens: (1) chain-like corrosion products (Fig. 8(d));

and (2) single crystals, all consisting of Fe-rich sulphides (Fig. 11).

Cracks in the alumina films are responsible for the chain-like corrosion products. Owing to these cracks in the alumina coating the aggressive gas components can reach the underlying metallic surface. The existence of the cracks is generally related to the internal stress in the thin oxide films [24]. Oxide films applied by MOCVD suffer in general from thermal and intrinsic stresses, according to:

$$\sigma_{\text{internal}} = \sigma_{\text{intrinsic}} + \sigma_{\text{thermal}}$$

These internal stresses may be generated by different sources: during film formation and/or owing to thermal mismatch. The thermally induced part of the stress in alumina on steel can be calculated from the difference between the thermal expansion coefficients of the film and the metal, the difference between the deposition and the actual temperature, and the Young's modulus of the film. The intrinsically induced part is caused by the growth mechanism of the amorphous alumina film.

(a)

(b)

Fig. 10. SEM image of the surface morphology of coated samples after 24 h of sulphidation at 450 °C showing Fe-rich sulphide products. Partial pressure of ATSB, (a) 5.33×10^{-3} kPa, (b) 2.67×10^{-2} kPa; deposition temperature, 400 °C.

Fig. 11. SEM image of the surface morphology of a coated sample after 24 h of sulphidation at 450 °C showing localised Fe-rich sulphide products. Deposition temperature, 400 °C; partial pressure of ATSB, 5.33×10^{-3} kPa.

The origin of the intrinsic stresses is yet unclear. Morssinkhof [25] reported that the large intrinsic stress may be explained by the presence of hydroxide groups

Fig. 12. SEM image of the surface morphology of a coated sample after 24 h of sulphidation at 450 °C, showing cracks near the edge of the specimen. Deposition temperature, 400 °C; partial pressure of ATSB, 2.67×10^{-2} kPa.

in the oxide scale. However, the relationship between the incorporation of elements or groups of atoms and the critical coating thickness is not yet clearly understood. Tucker [26] mentioned that the residual stress increased linearly with coating thickness but an exact mechanism explaining this relation was not formulated.

Crack formation was also found by Evans *et al.* [27], who reported that a curved substrate or a surface showing sinusoidal interfaces, will lead to an increased susceptibility to crack formation. This explains the existence of substantial shear and tensile stress concentrations near edges and film terminations (see also Fig. 12).

The porous structure of the alumina films, which was more pronounced for low than high deposition temperatures, can be explained by the low conversions of the metal alkoxides or incorporation of $\text{AlO}(\text{OH})$ or H_2O into the film. For example, Baryshnikov [28] reported that at low conversion of the metal alkoxides, the corresponding alcohol was identified in amounts of up to 1 mole per mole of the substance being decomposed. In a later stage the alcohol decomposes at the surface of the specimen.

To increase the protectiveness of the alumina coatings, a crack- and pore-free oxide film with reduced stresses should be produced. This can be obtained by, amongst others, the formation of an intermediate oxide layer between the coating and the metal, lowering of the deposition rate at high deposition temperatures, the incorporation of elements in the oxide lattice such as Si [29] which will result in a higher density of the film, and the addition of other compounds to the gas stream saturated with the precursor. Also, thermal annealing by a heat-treatment afterwards may result in reduced stresses [5, 30].

In the near future more research will be performed in order to obtain alumina films with well-defined chemical and mechanical properties.

4. Conclusions

Thin films of aluminium oxide can be obtained by pyrolytic decomposition of Al-tri-*sec*-butoxide. The activation energy for the heterogeneous reaction is 83 ± 5 kJ mol⁻¹. The surface morphology of the thin films, deposited on metallic substrates, showed cracks and a porous structure, which were more pronounced at low deposition temperatures. Eventhough the coated specimens are much less attacked than uncoated ones, the application of these layers for corrosion protection of the underlying metallic materials is as yet suffering from fast diffusion paths such as cracks and pores. The aggressive gas components can consequently easily reach the underlying substrate, forming, for example, sulphide products. Higher deposition temperatures, corresponding to the region of diffusion-limited film growth, leads to a less uniform but a more protective behaviour of the alumina film owing to a denser structure.

More research is necessary for the preparation of uniform thin alumina films with well-defined chemical and mechanical properties by several methods such as the addition of foreign elements, thermal annealing and the addition of other compounds to the gas stream.

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