

Organometallic Chemical Vapour Deposition in the Al–O–N System

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Abstract

Using chemical vapour deposition, aluminium–oxygen–nitrogen system coatings have been synthesized with trimethylaluminium, ammonia and nitrous oxide. The composition of the equilibrium phases is first determined by a thermodynamic calculation. The only Al–O–N phase investigated is (γ) spinel aluminium oxynitride and it is considered as a stoichiometric phase with the Al_7O_9N composition. The results indicate the existence fields of aluminium nitride and alumina, and show the difficulty of obtaining the spinel aluminium oxynitride without other phases. Temperature and pressure influence the equilibrium compositions because they directly modify the quantity of CO present. A cold-wall reactor is used for the experimental study. In this way AlN, a mixture of AlN and γ -AlON (γ -aluminium oxynitride), and α - Al_2O_3 are obtained. The annealed deposits show the stability of γ -AlON obtained at 1370 K.

Aus Trimethylaluminium, Ammoniak und gasförmigen N–O-Verbindungen wurden über ein CVD-Verfahren Schichten mit einer chemischen Zusammensetzung innerhalb des Al–O–N-Systems erzeugt. Die Zusammensetzungen der Gleichgewichtsphasen wurde zuerst über thermodynamische Berechnungen ermittelt. Die einzige Al–O–N-Phase, die im Rahmen dieser Arbeit untersucht wurde, entspricht dem γ -Aluminiumoxinitridspinel für dessen chemische Zusammensetzung die stöchiometrische Al_7O_9N -Phase angenommen wird. Die Ergebnisse zeigen die Existenzbereiche von AlN und Al_2O_3 auf und erklären ferner die Schwierigkeit, die Aluminiumoxinitridspinelphase phasenrein herzustellen. Temperatur und Druck haben über die Veränderung des CO-Anteils einen unmittelbaren

Einfluß auf die Gleichgewichtszusammensetzungen. Die Versuche wurden in einer Reaktionskammer mit gekühlten Wänden durchgeführt. Unter diesen Bedingungen erhielten wir als Reaktionsprodukte AlN, eine Mischung aus AlN und γ -AlON (γ -Aluminiumoxinitrid) und α - Al_2O_3 . Getemperte Niederschläge demonstrieren die Stabilität des bei 1370 K erhaltenen γ -AlON.

Des matériaux du système aluminium–oxygène–azote ont été obtenus par dépôt chimique en phase gazeuse à partir de triméthylaluminium, d'ammoniac et de protoxyde d'azote. Une étude thermodynamique nous a permis de déterminer la composition des phases en équilibre. Parmi les différents oxynitrides existants, seul l'oxynitride d'aluminium spinelle (γ) sera pris en compte et nous le considérerons comme une phase stœchiométrique de composition Al_7O_9N . Ces résultats nous indiquent les domaines d'existence d'AlN et Al_2O_3 et nous montrent la difficulté d'obtenir l'oxynitride d'aluminium spinelle exempt d'autres phases. La température et la pression agissent sur la composition à l'équilibre en modifiant la quantité de CO. L'étude expérimentale a été effectuée dans un réacteur à paroi froide. Nous avons ainsi élaboré AlN, un mélange de AlN et d'oxynitride d'aluminium spinelle (γ -AlON), et α - Al_2O_3 . Le recuit des dépôts nous montre la stabilité de l'oxynitride spinelle obtenu à 1370 K.

1 Introduction

Aluminium–oxygen–nitrogen system materials have many applications in electronics and as oxidation resistant products. The range of applications can be increased using CVD, so the Al–O–N system was investigated using this process. AlN¹ and Al_2O_3 ^{2,3}

coatings have been synthesized with this process but those of aluminium oxynitride have not been studied extensively.⁴ On the other hand, many studies of this system have been made but with sintered materials.⁵⁻⁷ Thus, in the pseudobinary AlN- α -Al₂O₃, three types of aluminium oxynitrides are seen:

- In the AlN-rich region the polytypes of AlN: 27R, 21R, 12H.
- The γ -spinel aluminium oxynitride, a solid solution, with wide composition range above 1970 K.
- Φ' -Aluminium oxynitride appears in the Al₂O₃-rich region of the diagram at high temperature.

The authors now consider the synthesis of these materials using chemical vapour deposition with trimethylaluminium (TMAI) ammonia and nitrous oxide.

2 Thermodynamic Study

The composition of the equilibrium phases is first determined by a thermodynamic calculation. The equilibrium calculation is based upon the Gibbs free energy minimization method in a closed system. The 'SOLGASMIX' program developed by Eriksson⁸ was used, which calculates both vapour- and solid-phase compositions when equilibrium is reached at a given temperature and total pressure. The deposit is considered to be in equilibrium with the vapour phase. It is assumed that the substrate is chemically inert with respect to the deposit and the vapour phase, and that all the chemical species which can be present in equilibrium are known and taken into account in the calculations.

With the precursors in this study the system Al-C-H-O-N is considered. Thus 57 species are considered (Table 1). The thermodynamic data used for the calculation are taken from JANAF⁹ tables, where possible, or from the tables produced by Barin & Knacke¹⁰ for CH₄O. Those concerning the organometallics have been studied by Tirtowidjojo & Pollard.¹¹

For the Al-O-N system species some assumptions have been based on the results of Kaufman¹² and Dorner *et al.*¹³ Both determined that the γ -aluminium oxynitride spinel phase is the only stable phase in the Al-O-N system below 2150 K and considered that the spinel phase is a stoichiometric phase with the Al₇O₉N composition. The difference between the Gibbs free energy of Al₇O₉N formation determined by these two authors is insignificant

Table 1. Chemical species introduced in the thermodynamic calculations (< > solid, // liquid, gas)

Al	<AlN>	CHN	H
Al(CH ₃) ₃	<Al ₄ C ₃ >	<C>	H ₂
Al(CH ₃) ₂	<Al ₂ O ₃ α >	N	H ₂ O
Al(CH ₃)	<Al ₇ O ₉ N>	N ₂	H ₂ O ₂
Al ₂ (CH ₃) ₆	CH ₄	NH ₃	HNO
AlH(CH ₃)	CH ₃	NH ₂	HNO ₂
AlH(CH ₃) ₂	CH ₂ O	NH	HNO ₃
AlH ₂ (CH ₃)	CH ₄ O	N ₂ H ₂	
AlH	CHO	N ₂ H ₄	
AlN	C ₂ H ₂	NO	
AlOH	C ₂ H ₄	NO ₂	
AlOOH	CO	NO ₃	
AlO	CO ₂	N ₂ O	
AlO ₂	CH ₃ OH	N ₂ O ₃	
Al ₂ O	CN	N ₂ O ₄	
Al ₂ O ₂	CHNO	O ₂	
/Al/	CNO		

above 1873 K but below this temperature the difference is important for evaluating the stability of aluminium oxynitride. In fact, the data from Dorner *et al.* project the oxynitride as unstable, whereas Kaufman's show it to be stable at room temperature. Kaufman's values were chosen because they are in better agreement with the experimental data.

Using the thermodynamic study, a large domain is considered for investigation whose parameter limits are: $10^{-2} \leq N_2O/Al(CH_3)_3 \leq 100$; $0 \leq NH_3/Al(CH_3)_3 \leq 1$; $1000 \leq T \leq 1800$ K; $10^{-3} \leq P \leq 1$ atm ($101 \leq P \leq 101\,325$ Pa). The chemical species initially introduced into the calculations either react totally at equilibrium to give new species or remain partially unreacted. The results are formulated as thermodynamic yield η_x , defined as the ratio between the mole number of species x and the mole number of the parent species, taking into account the stoichiometric coefficient. For example:

$$\eta_{AlN} = \frac{AlN_{eq}}{Al(CH_3)_3_{in}} \quad \eta_{Al_7O_9N} = 7 \frac{Al_7O_9N_{eq}}{Al(CH_3)_3_{in}}$$

$$\eta_{CO} = \frac{CO_{eq}}{3Al(CH_3)_3_{in}}$$

in which X_{in} is the input number of moles of species X and X_{eq} is the number of moles of species X at equilibrium.

2.1 Influence of the initial composition

The variations of η_x are considered as a function of the initial composition ratios $\alpha = Al(CH_3)_3/N_2O$ and $\xi = NH_3/Al(CH_3)_3$. The results with $\xi = 1$ are shown in Fig. 1. To explain the results two ratios, α and α^* , are considered, with

$$\alpha^* = \frac{Al(CH_3)_3_{in}}{(N_2O_{in} - CO_{eq})}$$

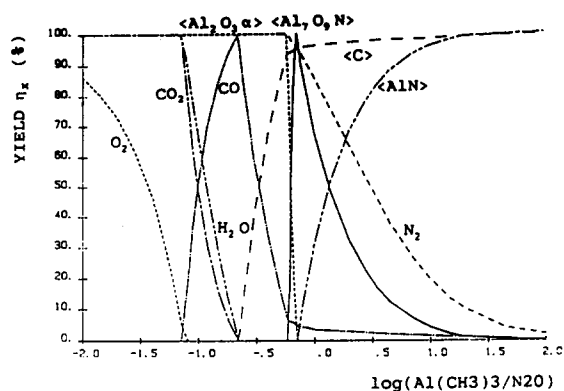


Fig. 1. Variation of η_x equilibrium yields for the main species as a function of α with $\xi=1$, $P=0.05$ atm (5066 Pa) and $T=1400$ K.

- When $\alpha^* \ll 2/3$, there is an excess of oxygen, and at equilibrium all the phases are in their most oxygenated state: Al_2O_3 , CO_2 , H_2O , O_2 .
- When $\alpha^* < 2/3$, firstly emergence of the less oxygenated gas phase such as CO is seen, then, as α^* increases, the CO quantity decreases, stabilizing at a low level.
- When $\alpha^* > 2/3$, there is not enough oxygen to produce alumina alone and a less oxygenated phase, $\text{Al}_7\text{O}_9\text{N}$, emerges. Thus, for $7/9 > \alpha^* > 2/3$, a mixture of $\text{Al}_7\text{O}_9\text{N}$ and Al_2O_3 is obtained.
- When $\alpha^* = 7/9$, pure $\text{Al}_7\text{O}_9\text{N}$ is obtained.
- When $\alpha^* > 7/9$, there is not enough oxygen to have pure $\text{Al}_7\text{O}_9\text{N}$, and as there is an excess of nitrogen there is emergence of AlN . Carbon always occurs in association with $\text{Al}_7\text{O}_9\text{N}$ and AlN .

The results with $\xi = 0$ are shown in Fig. 2. The η_x yields are the same as for the previous case up to $\alpha^* < 1$. The nitrogen now only comes from the nitrous oxide. Thus, when α^* is too big, there is not enough nitrogen in the mixture to make AlN alone. However, as there is an excess of carbon there is emergence of Al_4C_3 .

2.2 Influence of the temperature and total pressure

Thermodynamic calculations have been performed for a temperature and total pressure ranging from 1000 to 1800 K, and from 10^{-3} to 1 atm for $\alpha=1$ and $\xi=1$ (Figs 3 and 4). When for a given composition the pressure decreases or the temperature increases, the quantity of CO increases. Thus, if there is a mixture of two phases, the quantity of the least oxygenated phase increases at the expense of the most oxygenated one. The yields η_x , as a function of α for a different pressure $P=0.003$ atm (304 Pa; Fig. 5) and a different temperature $T=1600$ K (Fig. 6), show the pressure and temperature dependence—they directly influence the quantity of CO at equilibrium. So, for a ratio α defined, the ratio α^* is changed.

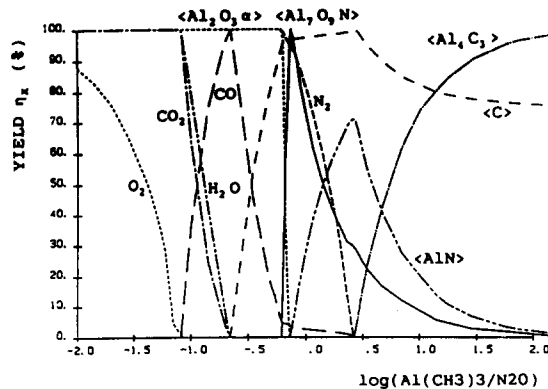


Fig. 2. Variation of η_x equilibrium yields for the main species as a function of α with $\xi=0$, $P=0.05$ atm (5066 Pa) and $T=1400$ K.

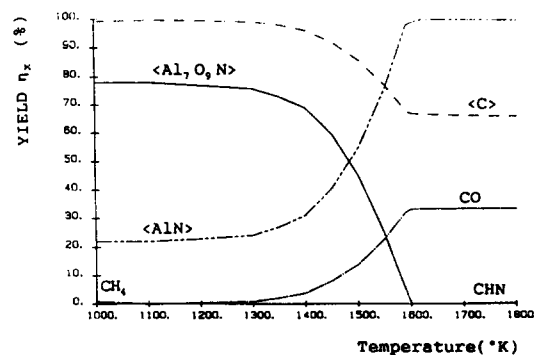


Fig. 3. Variation of η_x equilibrium yields for the main species as a function of temperature with $\xi=1$, $\alpha=1$ and $P=0.05$ atm (5066 Pa).

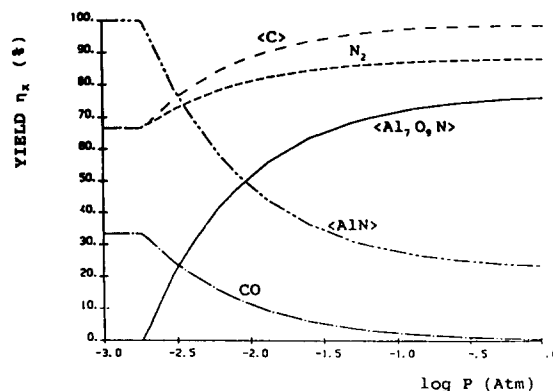


Fig. 4. Variation of η_x equilibrium yields for the main species as a function of pressure with $\xi=1$, $\alpha=1$ and $T=1400$ K.

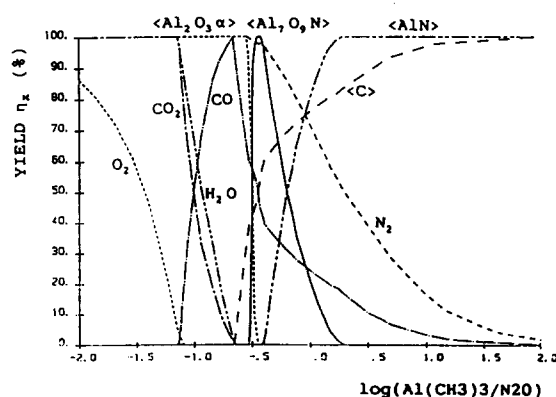


Fig. 5. Variation of η_x equilibrium yields for the main species as a function of α with $\xi=1$, $P=0.003$ atm (304 Pa) and $T=1400$ K.

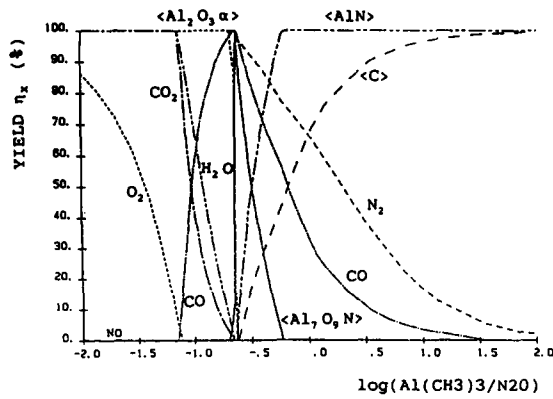
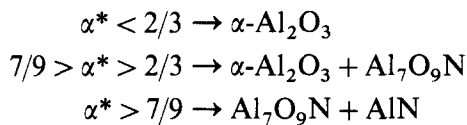


Fig. 6. Variation of η_x equilibrium yields for the main species as a function of α with $\xi=1$, $P=0.05$ atm (5066 Pa) and $T=1600$ K.

We still have



3 Experimental Study

The experimental equipment used is a vertical cold-wall reactor. The substrate, suspended in a silica glass tube reactor, is heated by high-frequency induction. A graphite substrate which reacts very quickly with oxygen is used so it has to be protected. In order to do this a thin layer of silicon carbide is deposited by chemical vapour deposition on it. The chemical stability of the substrate is thus improved. β -SiC is then deposited by CVD using tetramethylsilane (TMS) decomposition under the following conditions: $T=1623$ K, $P=4000$ Pa, $D_{\text{H}_2}=100$ cm³/min, $D_{\text{TMS}}=15$ cm³/min.¹⁴ A thickness of 20 μm is deposited in 30 min.

3.1 Aluminium nitride

The investigations are started without N_2O at $T=1370$ K and $P=133$ Pa. The ratio ξ was varied from 1 to 20. The X-ray diffraction pattern shows that there is AlN and that all the coatings are well crystallized (Fig. 7(a)). When $\xi \leq 5$ the coatings are non-homogeneous and do not adhere to the substrate, but when $\xi \geq 10$ homogeneous compact coatings are obtained. Scanning electron microscope (SEM) observations of the cross-section reveal that the coatings have high porosity (Fig. 8) which arises from a high-speed growth (nearly 30 $\mu\text{m}/\text{h}$). Good adherence between substrate and coating is also seen. With $\xi=10$ the influence of the total pressure and temperature on the coatings is investigated. These range respectively from 55 to 660 Pa and 1050 to 1670 K. For a temperature of 1050 K and a

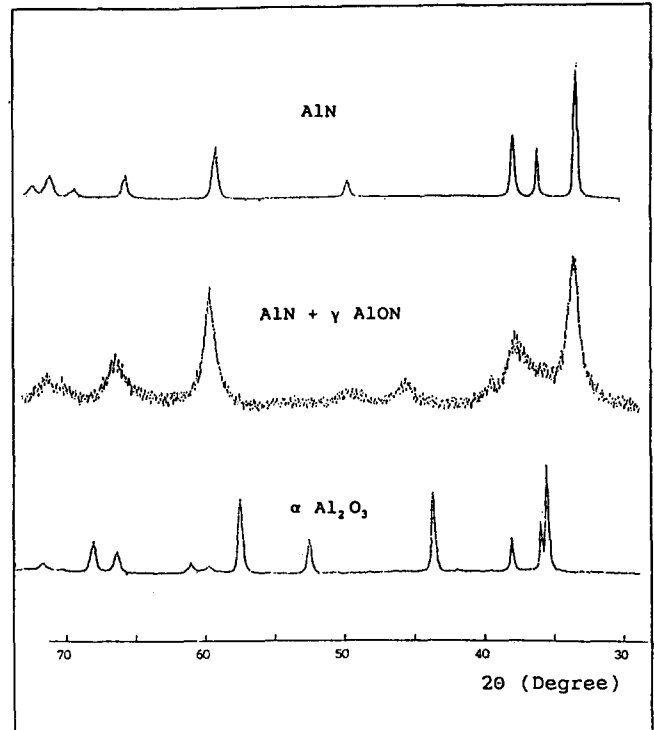


Fig. 7. X-Ray diffraction pattern of (a) AlN, (b) AlN and γ -AlON, and (c) α -Al₂O₃.

pressure of 133 Pa the coatings have the same morphology but are less crystallized than those obtained at 1370 K. In fact, broadened peaks are observed on the X-ray diffraction pattern. As the temperature increases the crystallization is better, but for $T=1670$ K the coating occurs as a columnar growth. At a temperature of 1370 K, for a lower pressure ($P=55$ Pa) the coatings are more homogeneous, but for a higher pressure ($P=660$ Pa) the coatings are not adherent and are powdered. This phenomenon is due to a gas-phase reaction. Trimethylaluminium is a very unstable product, so if the pressure is sufficient a gas-phase reaction occurs and induces a powdered deposit. Wavelength dispersive system (WDS) analysis indicates the presence of carbon (4–8%) and oxygen (2–6%).

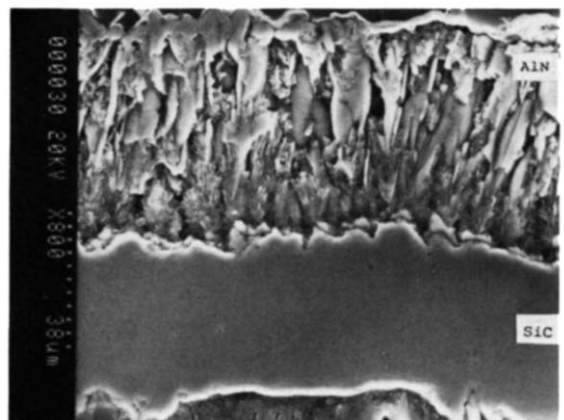


Fig. 8. SEM micrograph of a cross-section of AlN ($\xi=10$, $P=133$ Pa, $T=1400$ K, $D_{\text{N}_2\text{O}}=0$ cc/min).

3.2 Aluminium oxynitride

Nitrous oxide is now introduced into the reaction gas mixture. All the following studies are done with the conditions $\xi = 1$, $T = 1370$ K and $P = 133$ Pa. With a ratio of $N_2O/TMAI \geq 10$ homogeneous and compact coatings are obtained. X-Ray diffraction patterns indicate the emergence of γ -aluminium oxynitride; more precisely, there is a mixture of γ -AlON and AlN (Fig. 7(b)). To verify the existence of γ -AlON as opposed to γ -Al₂O₃ it is necessary to anneal the coatings—annealing transforms γ -Al₂O₃ into α -Al₂O₃. Thus all coatings are at 1370 K under 7×10^5 Pa of nitrogen for 2 h. The X-ray diffraction pattern of the annealed coatings shows well-defined peaks of γ -AlON. The coatings are thus stable.

The quantity of each phase of the mixture can be evaluated approximately from the ratio of the heights of the peaks corresponding to the two phases in the X-ray pattern. Thus, when $N_2O/TMAI$ increases, the quantity of γ -AlON is higher. WDS analysis confirms this phenomenon. The quantity of oxygen in the coatings is proportional to that of the N_2O input. These analyses indicate that there is less than 1.5% of carbon which is now in the CO phase. SEM shows non-porous coatings (Fig. 9) despite growth speeds of nearly 30 $\mu\text{m}/\text{h}$. Cracks are due to the presence of γ -AlON. Good adherence of the coating to the substrate is also seen. When the pressure increases from 55 to 660 Pa, the quantity of the γ -AlON phase in the mixture increases.

Subsequently the investigations are continued without ammonia. With $N_2O/Al(CH_3)_3 < 4$ an X-ray diffraction pattern corresponding to a mixture of α -Al₂O₃ and γ -AlON or γ -Al₂O₃ is obtained. These coatings are annealed under the same conditions as previously. Now, however, the γ -AlON or γ -Al₂O₃ disappears, and only peaks corresponding to α -Al₂O₃ remain. Thus, under these conditions, a

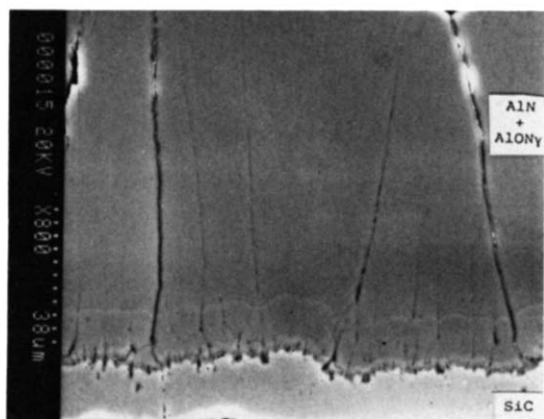


Fig. 9. SEM micrograph of a cross-section of a mixture of AlN and γ -AlON ($\xi = 1$, $P = 133$ Pa, $T = 1400$ K, $\alpha = 0.1$).

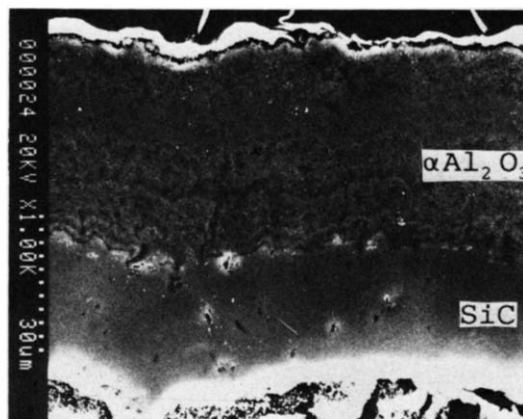


Fig. 10. SEM micrograph of a cross-section of α -Al₂O₃ ($\xi = 0$, $P = 133$ Pa, $T = 1400$ K, $\alpha = 0.2$).

mixture of γ -Al₂O₃ and α -Al₂O₃ is obtained. The emergence of γ -Al₂O₃ seems to be due to a stabilization of this structure by nitrogen.

3.3 Alumina

When the ratio of $N_2O/TMAI \geq 5$, a homogeneous deposit of well crystallized α -alumina (Fig. 7(c)) is obtained. SEM observations of the cross-section show that the coatings have a lower porosity (Fig. 10). WDS analysis indicates that they contain a lower quantity of nitrogen and carbon ($\leq 2\%$).

4 Conclusion

A thermodynamic study indicates the existence fields of AlN and Al₂O₃, and shows the difficulty of obtaining γ -AlON alone.

In the experimental study, by varying the quantity of ammonia and nitrous oxide, the entire Al–O–N system is explored. Thus AlN, a mixture of AlN and γ -AlON, and α -Al₂O₃ are consecutively synthesized. This study indicates that the spinel aluminium oxynitride can be obtained at 1370 K, using chemical vapour deposition, and these coatings are stable after being annealed at 1370 K.

The studies without NH₃ indicate that when nitrogen is only supplied as N₂O, γ -AlON cannot be obtained, but only γ -Al₂O₃ with nitrogen in solution is seen. This last result is the only one that is not in agreement with the thermodynamic calculations.

Acknowledgement

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