Journal of the European Ceramic Society **13** (1994) 339–344

An In-situ Study of the Oxidation of AlN Layers Fabricated by LPCVD Using X-Ray Diffraction

C. Labatut, D. Kharchi, B. Aspar, F. Sibieude & B. Armas

Institut de Science et de Génie des Matériaux et Procédés, BP 5, Odeillo, F-66125 Font-Romeu Cedex, France

(Received 5 July 1993; revised version received 10 October 1993; accepted 10 November 1993)

Abstract

AlN layers were elaborated on SiC substrates using the method of low-pressure chemical vapour deposition (LPCVD). The oxidation of these layers was studied in an X-ray diffraction chamber at temperatures between 900 and 1400°C with an oxygen flow (20 SCCM) at a pressure of 85 × 10^3 Pa.

The oxidation was followed as a function of time at several temperatures by observing the intensity of the diffraction peaks of the phases formed. At 1000°C, the action of oxygen leads to the formation of an oxynitride phase AlO_xN_y *indicated by the appearance of the (400) peak. Between 1000 and 1400°C, the oxidized phase is* α-Al_2O_3*, shown by the (012), (024) and (116) peaks. The kinetic elements thus obtained are discussed in terms of the morphology of the oxidized surfaces.*

AlN-Schichten wurden mit Hilfe der Niederdruck-Chemischen-Dampfniederschlag-Methode (LPCVD) auf ein SiC-Substrat aufgebracht. Die Schichten wurden in einer Röntgenbeugungskammer bei Temperaturen zwischen 900 und 1400°C und einem Sauerstoffstrom (20 SCCM) bei einem Druck von 85 × 10^3 Pa untersucht.

Die Entwicklung der Oxidation als Funktion der Zeit, bei verschiedenen Temperaturen, wurde anhand der Intensität der Beugungsreflexe bestimmt. Bei 1000°C bildet sich aufgrund der Anwesenheit von Sauerstoff eine Oxinitridphase, AlO_xN_y*, nachweisbar anhand der (400)-Reflexe. Zwischen 1000 und 1400°C besteht die Oxidphase aus* α-Al_2O_3*, nachweisbar durch die (012), (024) und (116) Reflexe. Die sich daraus ergebende Kinetik wird bezüglich der Morphologie der oxidierten Oberfläche diskutiert.*

Des revêtements de AlN ont été réalisés sur des substrats de SiC par la technique de dépôt chimique en phase gazeuse sous faible pression (LPCVD). Nous avons étudié l'oxydation des couches de AlN dans une chambre de diffraction de rayons X à des températures comprises entre 900 et 1400°C sous balayage d'oxygène (20 SCCM) à la pression de 85 × 10^3 Pa.

L'oxydation a été suivie en fonction du temps à plusieurs températures par l'intensité des pics de diffraction des phases formées. A 1000°C l'action de l'oxygène conduit à la formation d'oxynitrure AlO_xN_y *mis en évidence par l'apparition du pic (400). Entre 1000 et 1400°C la phase oxydée est* α-Al_2O_3*, mise en évidence par les pics (012), (024) et (116). Les éléments de cinétique ainsi obtenus sont discutés en relation avec la morphologie des surfaces oxydées.*

1 Introduction

Aluminium nitride (AlN) is a ceramic material interesting for its applications at high temperatures given its specific properties: high thermal conductivity; low expansion coefficient which gives it a good resistance to thermal shock and high stability at high temperature; good high resistivity and chemical inertness.[1–3]

The high-temperature oxidation resistance of this material is one of the reasons for its utilization.

However, the perfection of aluminium nitride by sintering necessitates the use of additives which lead to a weakening of the material at high temperature, due to the formation of vitreous phases.

In contrast, its elaboration by chemical vapour deposition (CVD) enables a dense, highly pure material to be obtained. In addition, this method lends itself to the fabrication of thin coatings which can be used to protect other materials against oxidation.

This aspect has been the object of many studies both on powders[4] and on sintered materials[5] and of course on films obtained using the plasma-enhanced chemical vapour deposition (PECVD) technique.[6,7] The latter method can lead to an aluminium nitride containing non-negligible quantities of hydrogen, as

Journal of the European Ceramic Society 0955-2219/94/$7.00 © 1994 Elsevier Science Limited, England. Printed in Great Britain

well as carbon, depending upon the type of precursor used.

In the present work, the AlN deposits were elaborated using CVD with a carbon-free halide as precursor.

The oxidation resistance of the AlN layers thus prepared was studied under a flow of oxygen, at high temperature, in a reaction chamber equipped with X-ray diffraction apparatus which enabled the radio-crystallographic evolution to be continuously followed.

2 Experimental Procedure

2.1 Material

To start with, it was necessary to prepare an aluminium nitride coating.

The experiments, carried out in a hot-wall CVD reactor, were based on reactions between aluminium chloride, $AlCl_3$, and ammonia, NH_3. The aluminium source, $AlCl_3$ vapour, was supplied by evaporation of solid $AlCl_3$ at 80°C.

The aluminium chloride vapour and ammonia, both diluted with nitrogen, were transported in separate inlet tubes, so that the two gases were mixed only after entry into the reaction chamber, to avoid the formation of complexes.[8]

Substrates were made of industrial silicon carbide coated with a β-SiC layer deposited by CVD using a tetramethylsilane (TMS) precursor to avoid the diffusion of impurities during the AlN oxidation. The substrate size was $7 \times 75 \times 2$ mm.

The substrate temperature was measured using an optical micropyrometer.

The SiC deposition parameters were:

—Total pressure, 130 Pa.
—Substrate temperature, 1200°C.
—Ratio $H_2/TMS = 40$.

The AlN deposition[9] parameters were:

—Total pressure, 130 Pa.
—Substrate temperature, 1000°C.
—Experimental ratios $NH_3/AlCl_3 = 1$ and $N_2/AlCl_3 = 240$.

The AlN coatings were characterized by X-ray diffraction (Fig. 1) and scanning electron microscopy (Fig. 2). The diffractograms obtained showed that the AlN deposits were well crystallized and did not present any preferential orientation: the diffraction peaks are well-defined and their intensity corresponds approximately to those of a powder diagram given in the ASTM cards.[10]

The examination of the surface using a scanning electron microscope (SEM) shows (Fig. 2) a deposit constituted of facetted micro-crystals. These crystals have a laminar form which can be interpreted from the theoretical morphology which was determined in a previous work.[11] This non-equilibrium form is induced by a growth rate for the (100) and (101) faces which is significantly faster than for the (001) face. The presence of arbitrarily oriented microcrystals confirms that the deposit is not preferentially oriented.

Cross-section micrographs exhibited a highly dense deposited material. The microcrystals have a relatively important size (of the order of 2 μm). In view of oxidation tests, 15-μm thick AlN layers were prepared.

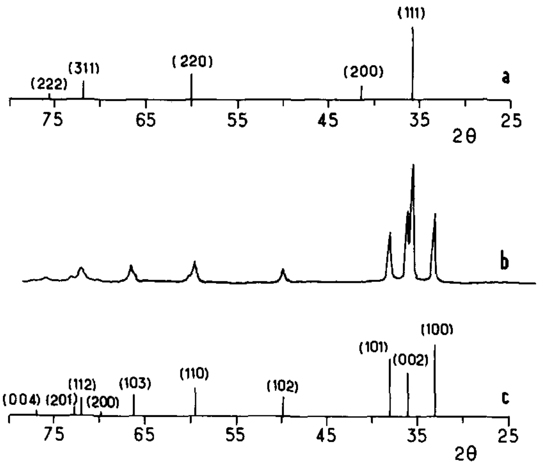


Fig. 1. X-Ray diffraction patterns of: (a) SiC powder, (b) CVD AlN, (c) AlN powder.

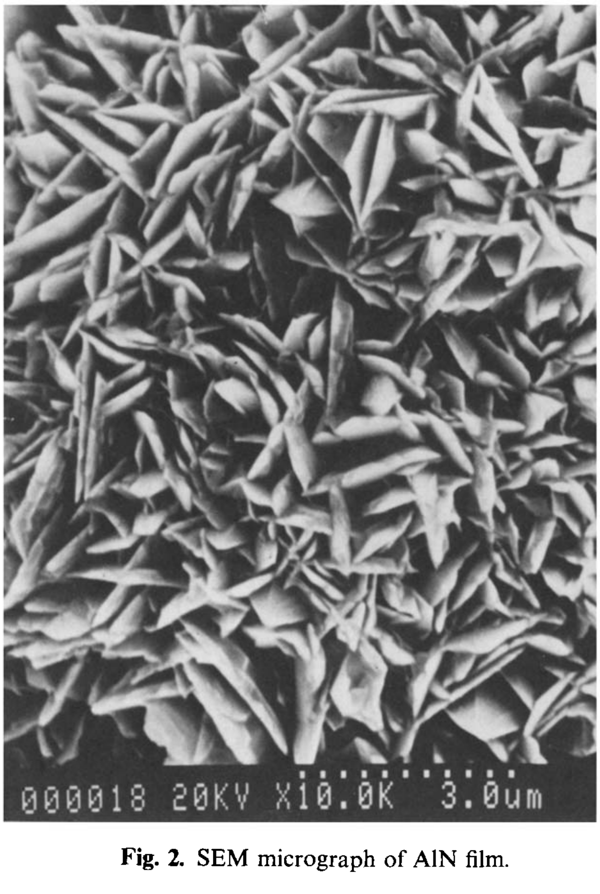


Fig. 2. SEM micrograph of AlN film.

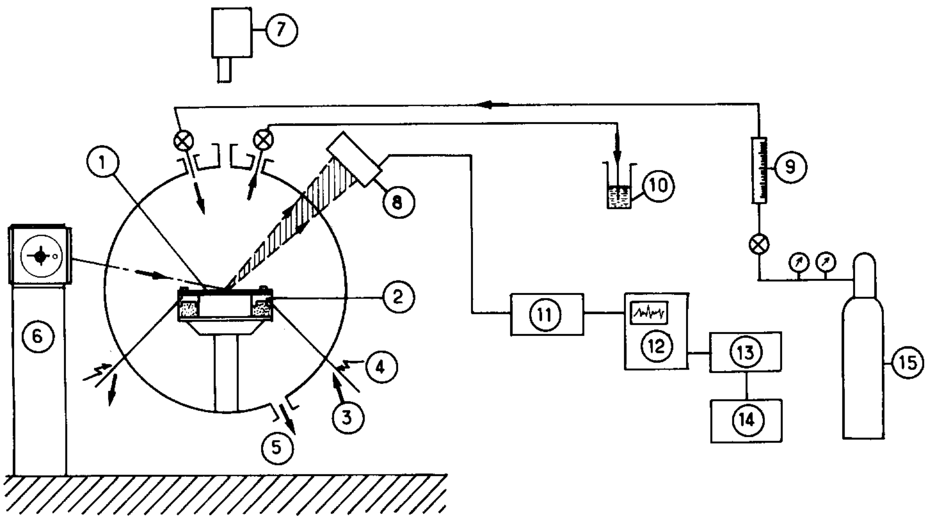


Fig. 3. Experimental apparatus for X-ray diffraction: 1, sample; 2, copper support; 3, cooling circuit; 4, electrical circuit; 5, vacuum pump; 6, X-ray source; 7, micropyrometer; 8, linear detector; 9, flowmeter; 10, bubbler; 11, electrical detection system; 12, multichannel analyser; 13, computer; 14, printer; 15, oxygen bottle.

2.2 Oxidation tests

The oxidation was carried out in a sealed X-ray diffraction chamber having two Mylar windows permitting the passage of the diffracted X-ray beam (Fig. 3). The sample was fixed directly onto the electrical terminals which were cooled copper blocks. The heating of the sample was by the Joule effect. A primary pump created the vacuum in the chamber. The oxygen was introduced subsequently and its flow was controlled. The pressure was maintained constant at 85×10^3 Pa. The sample temperature was measured with the aid of an optical micropyrometer. The peak heights were followed with a linear detector: portions of the diffractograms ($\Delta 2\theta = 12$ degrees) were recorded at regular time intervals giving the kinetic information. A geometry with low incidence (5 degrees) was selected to increase the X-ray path length in the material.

3 Calculation of the Oxidized Layer Thickness

The calculation of the thickness of the oxide makes use of the X-ray absorption of the oxidation layer on the AlN substrate (Fig. 4),[12] and the resulting intensity variations.

At a point A, the intensity of the incident ray is:

$$I_A = I_0 \exp(-\mu_{ox} EE' - \mu_s E'A) \qquad (1)$$

with I_0 = intensity of incident ray (XRi) before absorption, μ_{ox} = mass absorption coefficient of the oxidation layer and μ_s = mass absorption coefficient of the substrate. Segments EE' and $E'A$ are represented on Fig. 4.

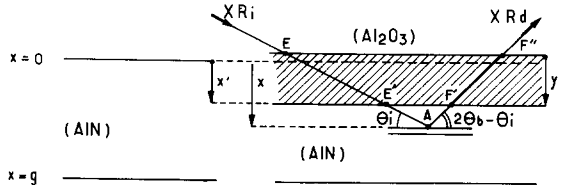


Fig. 4. (left) Coating before oxidation, (right) coating after oxidation.

The ray diffracted (XRd) by a volume element $\mathrm{d}V$ defined by $\mathrm{d}V = (hl\mathrm{d}x/\sin\theta_i)$ is expressed by:

$$\mathrm{d}I''_F = KI_0 lh/\sin\theta_i \exp[-(1/\sin\theta_i + 1/\sin\theta_s)(\mu_s(x - x') + \mu_{ox} y)]\,\mathrm{d}x \qquad (2)$$

with K = constant, l = beam width, h = length of volume element, θ_i = angle of incidence, θ_s = angle of diffraction with $\theta_s = 2\theta_b - \theta_i$ (θ_b = Bragg angle), y = thickness of the oxidation layer, x = depth of point A, x' = position of the AlN–Al_2O_3 interface, and g = thickness of AlN layer.

After integrating between x' and g and putting $A = (1/\sin\theta_i + 1/\sin\theta_s)$, the intensity of the diffracted ray at the exit from the material can be expressed in the form:

$$I''_F = KI_0 lh/\sin\theta_i \exp(-A\mu_{ox} y)\; 1/A[1 - \exp[-A(g - x')\mu_s]] \qquad (3)$$

At the beginning of the experiment $y = 0$ and $x' = 0$. The initial intensity $I''_F(0)$ can be expressed as:

$$I''_F(0) = KI_0 lh/\sin\theta_i \; 1/A[1 - \exp(-A\mu_s g)] \qquad (4)$$

It can be shown that in this particular case oxidation does not affect the total thickness of the layer and therefore $x' = y$. Then

$$B.C = \exp(-A\mu_{ox} y) - \exp[-A(\mu_s g + (\mu_{ox} - \mu_s) y)] \qquad (5)$$

with $B = 1 - \exp(-A\mu_s g)$ and $C = I''_F/I''_F(0)$.

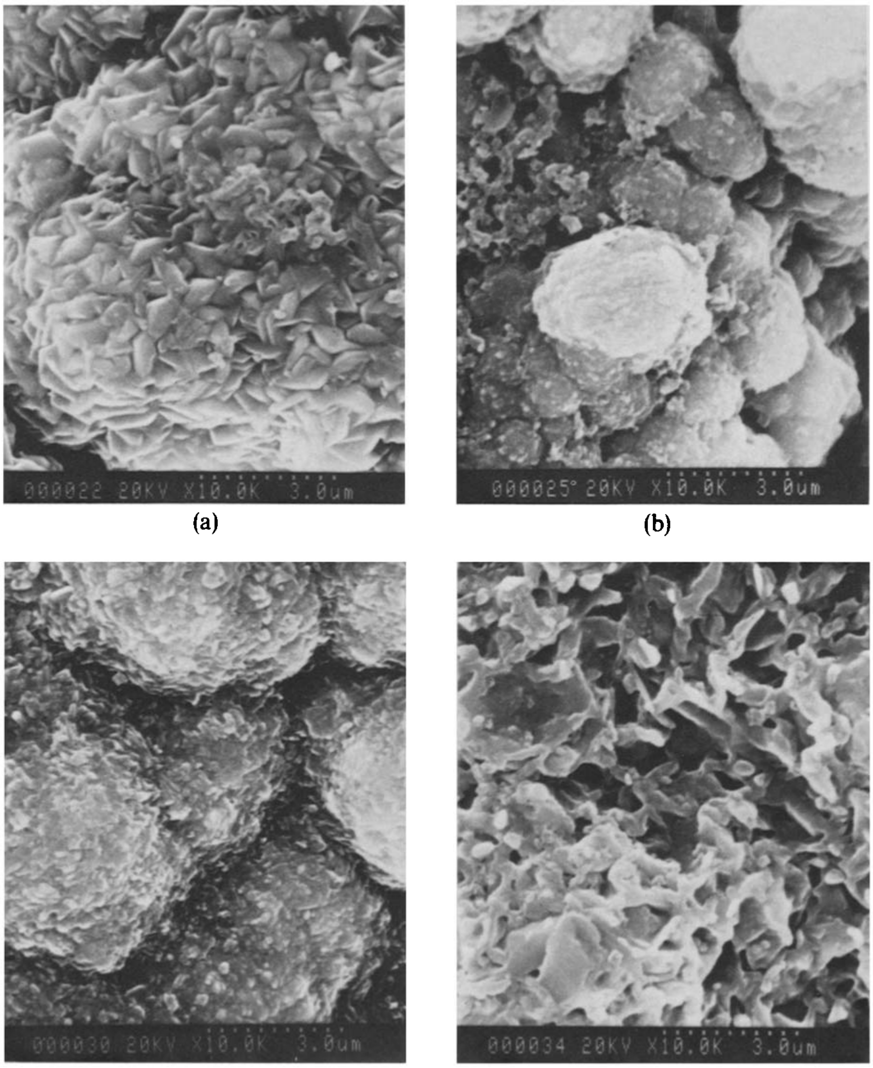
The numerical resolution of this equation gives the thickness y.

Using eqn (5) and the experimental measurement of intensity I''_F as a function of time gives the thickness as function of time.

4 Results and Discussion

4.1 Diffractograms and morphology

The samples of AlN were oxidized between 900 and 1400°C in an oxygen flow of 20 SCCM at 85×10^3 Pa.



(a) (b) (c) (d)

Fig. 5. SEM micrographs of AlN films after oxidation: (a) $T = 900°C$, (b) $T = 1000°C$, (c) $T = 1200°C$, (d) $T = 1400°C$.

At 900°C and for an oxidation lasting 13 h, the diffractograms obtained only show the characteristic peaks of AlN; no oxidized phase is detected.

The morphology of the surface observed by SEM revealed a surface deposit slightly different to that of AlN before oxidation (Fig. 5(a)). The crystallization nevertheless remains well-defined with laminar crystals embedded into each other.

At 1000°C, the diffractograms show, in the interval $2\theta/41$–52 degrees, a continuous evolution as a function of time (Fig. 6). A first oxidized phase of the AlO_xN_y type appeared during the first minutes of oxidation. After some further time, α-Al_2O_3 appeared. The coexistence of these three phases persisted until the end of the experiment. The surface morphology showed a very different aspect to that of the AlN at the start. The deposit seemed to be formed of globular masses having a badly defined crystallization. These globules were of the order of 2 to 3 μm in size (Fig. 5(b)). Figure 7 shows the diffractogram obtained after 24 h of oxidation. It seems that the AlO_xN_y phase disappeared to the profit of alumina. The AlN was always present.

At 1200°C, the diffractograms obtained in the $2\theta/45$–60 degree interval showed a continuous transformation of AlN into α-Al_2O_3 (Fig. 8). The surface morphology of this alumina was similar to that obtained during oxidation at 1000°C but the globule size was larger (3 to 4 μm) (Fig. 5(c)).

At 1400°C, the evolution of the phases in the interval $2\theta/20$–35 degrees was analogous to that obtained at 1200°C but the transformation was faster (Fig. 9).

In fact, the diffractogram obtained after 11 min oxidation revealed the presence of α-alumina uniquely.

The surface morphology of the alumina formed was quite different in this case. The crystallization was in the form of branches with numerous ramifications. This structure leads to an alumina which is much more porous (Fig. 5(d)).

4.2 Thickness of the layer formed by oxidation

The calculation of the variation of the formed layer as a function of time during the isothermic oxidations at 1000, 1200 and 1400°C leads to the

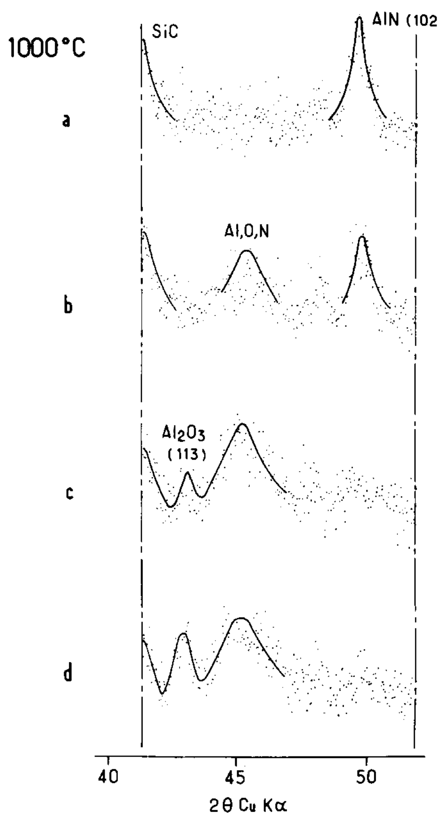


Fig. 6. Isothermic diffractograms (2θ-CuK_α) which show the evolution of the AlN, AlO_xN_y and Al_2O_3 peaks at $P_{O_2} = 85 \times 10^3$ Pa and $T = 1000°C$: (a) $t = 0$ min, (b) $t = 28$ min, (c) $t = 115$ min, (d) $t = 376$ min.

kinetic curves of Fig. 10. From it one can deduce a slow parabolic oxidation at 1000°C, a rapid parabolic oxidation at 1200°C and a linear oxidation at 1400°C.

Between 1000 and 1400°C, the square of the thickness as a function of time can be fitted to a straight line whose slope K_p increases with temperature:

$$K_p\ (1000°C) = 0{\cdot}064\mu^2/\text{min}$$
$$K_p\ (1200°C) = 2{\cdot}380\mu^2/\text{min}$$

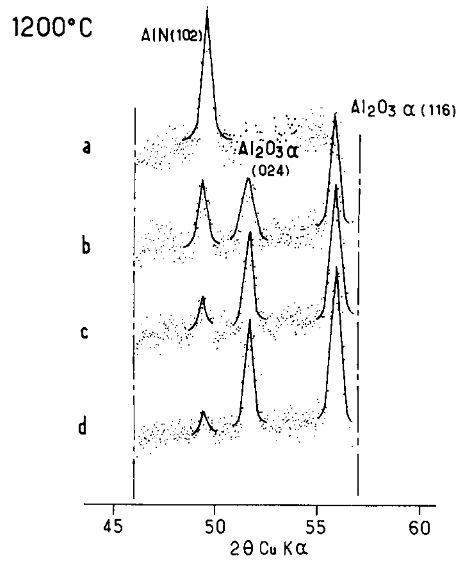


Fig. 8. Isothermic diffractograms (2θ-CuK_α) which show the evolution of the AlN and Al_2O_3 peaks at $P_{O_2} = 85 \times 10^3$ Pa and $T = 1200°C$: (a) $t = 0$ min, (b) $t = 11$ min, (c) $t = 21$ min, (d) $t = 40$ min.

The parabolic form of the growth of the oxidation layer indicates a reaction limited by the diffusion of oxygen across the oxide layer.

At 1400°C, the linear form of the curve and the rapidity of oxidation indicate a surface process limited by the chemical reaction. This would explain that in this case diffusion is not the limiting process.

4.3 Discussion

The oxidation of AlN coatings follows qualitatively the same kinetic laws as that of pulverulent or sintered materials. The faster growth observed here is due to a reaction mixture which is richer in oxygen ($P_{O_2} = 85 \times 10^3$ Pa) than in the cited works (oxidation in air). The oxidation resistance is analogous, that is to say that at temperatures below 1000°C, AlN is very little affected by oxidation.

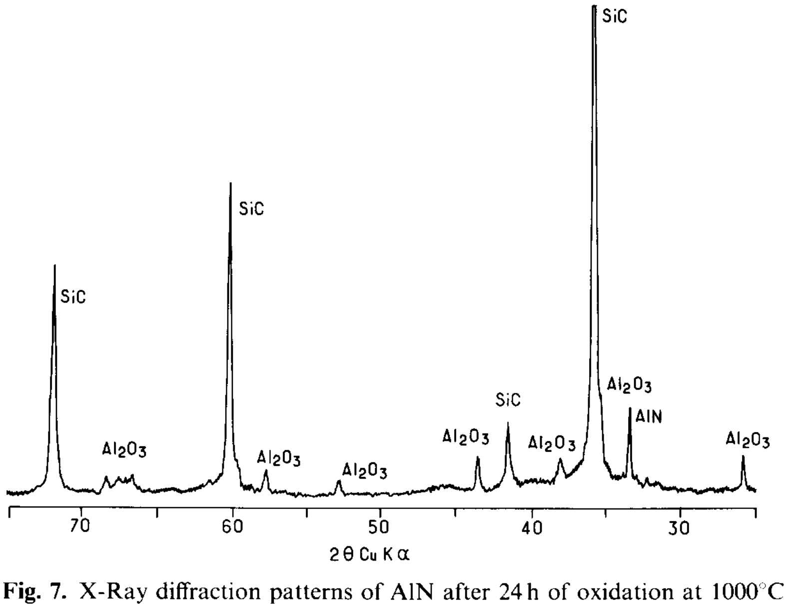


Fig. 7. X-Ray diffraction patterns of AlN after 24 h of oxidation at 1000°C.

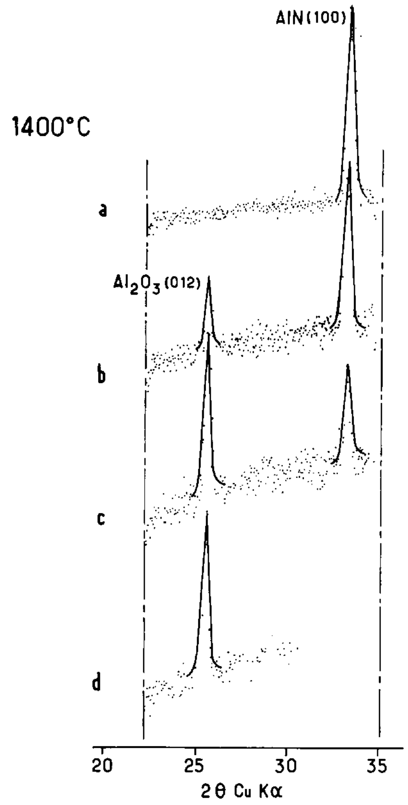


Fig. 9. Isothermic diffractograms (2θ-CuK_α) which show the evolution of the AlN and Al_2O_3 peaks at $P_{O_2} = 85 \times 10^3$ Pa and $T = 1400°C$: (a) $t = 0$ min, (b) $t = 4$ min, (c) $t = 9$ min, (d) $t = 11$ min.

The intermediate formation of an oxidation compound of the type AlO_xN_y noted previously is confirmed here by in-situ analysis.

5 Conclusion

The behaviour under oxidation of an AlN coating deposited on silicon carbide by LPCVD has been studied in the temperature range 900 to 1400°C.

With the method used, oxidation is only detectable above 1000°C, when a compound of AlO_xN_y type and α-alumina is formed. Above this temperature, the oxidation of the samples leads to the formation of α-alumina. The oxidation rate passes from a parabolic to a linear regime.

The phenomena observed are analogous to those occurring with solid materials prepared by sintering. One can therefore consider the use of this material in the form of layers in an oxidizing atmosphere at temperatures up to but not exceeding 1000°C.

Finally it should be noted that the nature of the substrate has been chosen considering its good compatibility with AlN, especially concerning thermal expansion coefficients.

Acknowledgements

This work has been partially supported by Aerospatiale, Division Systèmes Stratégiques et Spatiaux, F-33165 Saint-Medard-en-Jalles.

References

1. *Engineering Properties of Selected Ceramic Materials.* American Ceramic Society, Columbus, Ohio, 1966.
2. Zirinsky, S. & Irene, E. A., Selective studies of chemical vapor-deposited aluminium nitride–silicon nitride mixture films. *J. Electrochem. Soc.*, **125** (1978) 305.
3. Sakai, T. & Watanabe, A., *Amer. Ceram. Soc. Bull.*, **59** (1980) 853.
4. Katnani, A. D. & Papathomas, K. I., Kinetics and initial stages of oxidation of aluminium nitride: thermogravimetric analysis and X-ray photoelectron spectroscopy study. *J. Vac. Sci. Technol. A*, **5**(4) (1987) 1335–40.
5. Billy, M., Jarriche, J., Lecompte, J. P., Mexmain, J. & Yefsah, S., Comportement à l'oxydation du nitrure d'aluminium fritté. *Rev. Chim. Min.*, **19** (1982) 673–83.
6. Azema, N., Durand, J., Berjoan, R., Dupuy, C. & Cot, L., Oxidation stages of aluminium nitride thin films obtained by plasma-enhanced chemical vapour deposition (PECVD). *J. Eur. Ceram. Soc.*, **8** (1991) 291–8.
7. Ansart, F. & Bernard, J., Infrared optical properties of aluminium oxynitride films. *Phys. Stat. Sol.* (*a*), **134** (1992) 467–73.
8. Pauleau, Y., Hantzpergue, J. J. & Remy, J. C., Les couches minces de nitrure d'aluminium. *Bull. Soc. Chim. France*, **5–6**, (1979) 199–214.
9. Aspar, B., Armas, B., Combescure, C. & Thenegal, D., Chemical vapour deposition of the Al–O–N system. *J. Phys. IV, C2, Suppl. II*, **1** (1991) 665–72.
10. American Society for Testing Materials, Card No. 10-425.
11. Aspar, B., Rodriguez-Clemente, R., Figueras, A., Armas, B. & Combescure, C., Influence of the experimental conditions on the morphology of CVD AlN films. *J. Cryst. Growth*, **129** (1993) 56–7.
12. Rodriguez-Viejo, J., Contribution al estudio de la cinetica de oxidacion de SiC elaborado por CVD y analisis del comportamiento difusional del oxigeno en SiO_2. Doctoral thesis, UAB, Barcelona, Spain, 1992.

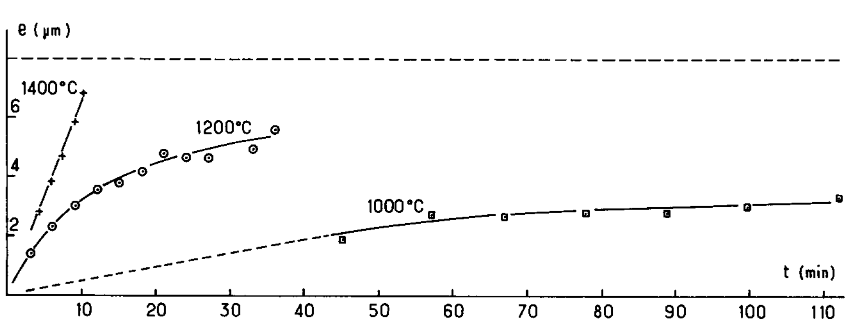


Fig. 10. Kinetic oxidation curves at different temperatures.