

Effect of Oxygen on the Thermal Conductivity of Aluminium Nitride Ceramics

J. Jarrige,^a J. P. Lecompte,^a J. Mullett^a and G. Müller^b

^aLaboratoire de Matériaux Céramiques et Traitements de Surfaces (LMCTS) URA CNRS 320, Faculté des Sciences, 123, avenue Albert Thomas, 87060 Limoges, Cedex, France

^bFraunhofer-Institut für Silicatiforschung, Neunerplatz 2, D-97082 Würzburg, Germany

Abstract

Sintered aluminium nitride is a good thermal conductor which is one of the principal properties of this ceramic. Previous studies have shown that the thermal flux transfer depends strongly on the oxygen contained in the crystal lattice, and on the powder surface. An AlN ceramic containing YF₃ as additive has been fabricated by tape-casting and sintering. This study shows that binder burnout must be carried out in air at 550°C or in nitrogen at 650°C. Sublimation of YF₃ to YOF, and formation of yttrium aluminate occurred during calcination. The amount of YF₃ present, thermal treatment duration and the rate of temperature increase and decrease affected oxygen diffusion in the nitride lattice. However, there is no correlation between thermal conductivity and oxygen content and microstructural characteristics are more influential than total oxygen content up to a thermal conductivity value of 220 W/mK. Published by Elsevier Science Limited.

Résumé

Le nitrure d'aluminium fritté est une céramique dont l'une des propriétés est d'être conductrice de chaleur. Les études antérieures ont montré que le transfert du flux de chaleur dépendait fortement de l'oxygène contenu dans le réseau cristallin mais aussi dans les poudres utilisées. Une poudre de nitrure d'aluminium a été frittée avec l'ajout YF₃ après avoir été mise en forme par coulage en bande. L'étude montre que le déliantage doit être conduit à 550°C à l'air, mais à 650°C sous atmosphère d'azote. Le suivi de cette réaction met en évidence la volatilisaton de YF₃, puis sa transformation en YOF, et la formation des aluminates. Le pourcentage en YF₃, la durée de traitement thermique et les vitesses de montée et descente en température interviennent sur la migration de l'oxygène dans le nitrure. Par contre pour les teneurs

mesurées, il n'apparaît pas de corrélation avec la conductivité thermique. Il semble plutôt que la microstructure occulte les effets de l'oxygène jusqu'aux valeurs de 220 W/mK.

1 Introduction

Aluminium nitride has a potential as an alternative material to alumina and beryllia currently in use in microelectronic devices.^{1–3} Its properties such as high thermal conductivity and a thermal expansion coefficient equivalent to that of silicon, have made AlN an important material for microelectronic packages and substrates. The highest value for thermal conductivity, 320 W/m k⁻¹, has been measured on a single crystal⁴ but the values obtained for commercial AlN are in the range 160–200 W m⁻¹ k⁻¹.^{5–7} One of the differences between single crystals and polycrystalline ceramic is that the heat carrier, i.e. phonons, propagate differently in each lattice. As a result of impurities or lattice defects in polycrystalline ceramics, phonon scattering may occur which leads to a decrease in thermal conductivity. Oxygen is one such impurity of polycrystalline AlN. Oxygen atoms occupy nitrogen sites and create aluminium vacancies to balance the electric charge.^{8,9} Oxygen is a typical contaminant of AlN, located at the surface of the AlN grains as aluminium oxide or oxynitride.¹⁰ During the sintering, oxygen reacts with the additive to form aluminates. Some AlN densified ceramics are obtained with sintering additives such as Y₂O₃ or CaO^{11,12} in the range 1800–1900°C. Some aluminate secondary phases are formed with Y₂O₃ additive, and identified as Y₃Al₅O₁₂ (YAG), YAlO₃ (YAP), Y₄Al₂O₉ (YAM), and also the oxide Y₂O₃. These phases are located around the AlN grains, along the grain edge, or in the triple

points depending on temperature,^{13–16} and the additive content. The aim of this work is to investigate the effects of YF₃ additions on the phase composition, oxygen contents and thermal conductivity of tape-cast AlN ceramics.

2 Experimental Procedure

2.1 Ceramic processing

Aluminium nitride ('Elf Atochem' A2, oxygen = 1.25 wt%) was mixed with yttrium fluoride ('Aldrich') and methylethylketone-ethanol in a ball mill. A phosphoric ester (C103 'Beycostat') was added to increase the dispersion. The slurry is tape-cast. The green bodies were dried for 24 h and cut in samples (30*30*1 mm). Binders were removed in air, or in nitrogen atmosphere between 200 and 800°C for 2 h as dwell time (heating and cooling rate 3°C min⁻¹). The samples were sintered in a graphit heater furnace at 1850°C in the range 1–8 h under nitrogen dynamic atmosphere (heating and cooling rate 2°C min⁻¹).

2.2 Characterization

The densities of the AlN ceramics were measured with a water picnometer. Their different phases were identified by XRD (Philips diffractometer PW 1730) after grinding, or on the surface of the substrates. Oxygen analyses were performed with a hot gas extraction analyser (TC-436, 'LECO Co'). It has been possible to identify the three types of oxygen present in the ceramic with a method developed by G. Müller:¹⁷ oxygen adsorbed at the surface of the grains (type I); oxygen of the secondary phase (type II); oxygen contained in the grains (type III). The thermal conductivity was directly measured by the Fourier Law, with an apparatus developed by 'CNET' and Nantes University on a small bar 28*1,9*1,9 mm.

3 Results

3.1 Influence of the pyrolysis and the sintering atmospheres

Whatever the atmosphere, the decomposition of the organic phases is completed at 400°C and presents a weight loss of 8.5%, then the loss is stable in the range 400–600°C. Yet two different reactions are obtained after 600°C with the atmosphere: the

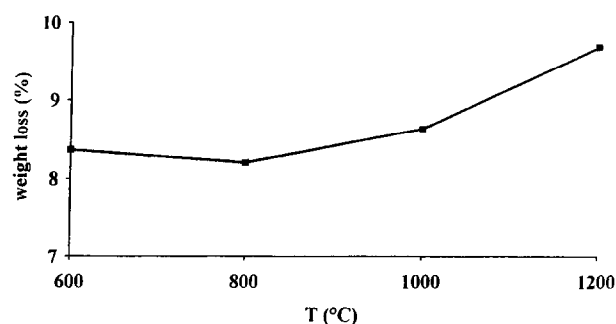
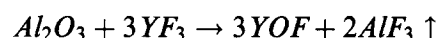


Fig. 1. Weight loss versus temperature of AlN green sheets in nitrogen atmosphere (4 wt% YF₃).

AlN oxidation¹⁸ is in competition with the decomposition of yttrium fluoride. When the pyrolysis is realised with an air flow, the oxidation is dominant, so a weight rise of the sheet of 2% is observed. Yet, YF₃ decomposes in YOF at 600°C and is transformed in Y₂O₃ at 800°C. With the nitrogen atmosphere, no weight rise is noticed (Fig. 1): there is neither oxidation nor YF₃ decomposition in the range 600–800°C. This last is obtained during the sintering with a temperature above 1000°C: YOF appears at 1100°C and the aluminate at 1400°C. In fact YF₃ reacts with Al₂O₃ deposited on AlN grain surface to form YOF



Some thermodynamic studies show that this reaction is a solid–gas reaction, and that YF₃ is vaporized before the reaction with alumina. The formation of the aluminate is obtained between 1100 and 1400°C by reaction with YOF.

3.2 Influence of the yttrium fluoride content

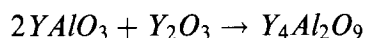
Different sheets were sintered at 1850°C for 1 h with various amounts of additive (1 to 10 wt%) and all samples presented a densification rate above 98%. We also noticed that the weight loss increases with the YF₃ content (8–16 wt%). The analyses of sintered translucent substrates reveal that, on the one hand no fluor is detected and on the other hand different aluminates are identified (Table 1): YAP (YAlO₃) and YAM (Y₄Al₂O₉). Some YAP phases are formed with a low YF₃ content, and mixtures, respectively, of YAP/YAM and YAM/Y₂O₃ are obtained by increasing the YF₃ amount first from 3–8 wt% YF₃ and then to 10 wt% YF₃. The rise of YF₃ content allows the formation of Y₂O₃ which reacts with the aluminate phase to produce a richer yttrium aluminate phase

Table 1. Aluminate phases observed by XRD versus YF₃ contents in AlN substrates sintered at 1850°C, 1 h

% YF ₃	1	2	3	4	5	6	8	10
Phases	YAP	YAP	YAP (YAM)	YAP YAM	YAP YAM	YAM (YAP)	YAM YAP	YAM Y ₂ O ₃

Table 2. Oxygen contents (wt%) versus YF₃ percentages measured in AlN substrates sintered at 1850 C, 1 h

% YF ₃	O (total)	O(II)	O(III)
1	0.67	0.48	0.19
2	0.89	0.69	0.2
3	0.95	0.77	0.18
4	1.02	0.89	0.13
5	1.36	1.28	0.08
6	1.39	1.34	0.05
8	1.77	1.7	0.07
10	2.0	2.0	0



The oxygen analyses reported in Table 2 show that the total oxygen content increases with the YF₃ content whereas intragranular oxygen (OIII) decreases and intergranular oxygen (OII) increases. The SEM observations (Fig. 2) show that the repartition of the secondary phases is the same for all the percentages of YF₃: triple points and edges of the grains. The AlN grain shape is polygonal, but there is a size evolution with the YF₃ content: 8–10 μm for 1 wt% YF₃, 5–10 μm for 4 wt% YF₃, 3–5 μm for 6 wt% YF₃ and inferior to 3 μm for

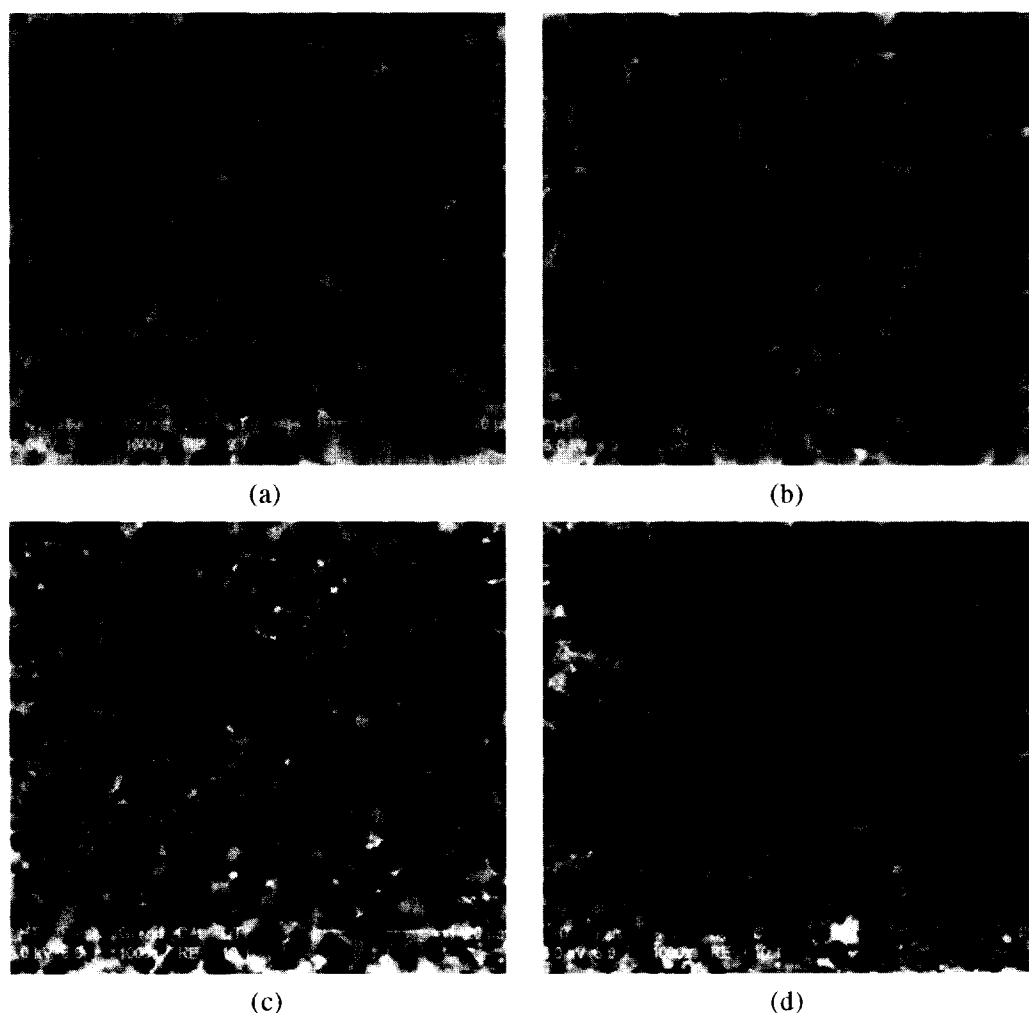
Table 3. Aluminate phases observed by XRD versus annealing time in AlN substrates sintered at 1850°C

Dwell time (h)	1	2	3	4	5	6	8
Phases	YAM	YAM	YAM	YAM	YAM	YAM	YAM
	YAP	YAP	YAP	YAP	YAP	YAP	YAP

10 wt% YF₃. Figure 3 shows that the maximum of the thermal conductivity (200 W min⁻¹ K⁻¹) is obtained with 4 wt% YF₃ and it stabilizes after 6% wt YF₃. These results allow the deduction that 4 wt% YF₃ is the more interesting additive content for the following studies.

3.3 Influence of the thermal treatment times

Some substrates are prepared at 1850°C with 4 wt% of YF₃ and various annealing times (1–8 h). The densification rates are maximum whatever the annealing time and the weight losses are all equal to 12 wt%. The secondary phases detected by XRD are reported in Table 3. They show that time has no influence on their nature. The SEM observations show (Fig. 4(a)) that secondary phases are located at the triple points, on the edges of the grains with some low dwell times. The AlN grains

**Fig. 2.** SEM of AlN substrates sintered at 1850°C, 1 h versus YF₃ contents. ((a): 1 wt%, (b): 4 wt%, (c): 6 wt%, (d): 10 wt%).

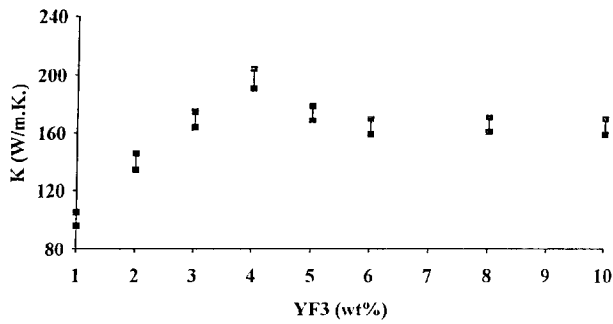


Fig. 3. Thermal conductivity versus YF_3 contents in AlN ceramic sintered at 1850°C , 1 h.



(a)



(b)



(c)

Fig. 4. SEM of AlN ceramics sintered at 1850°C , 4 wt% YF_3 versus annealing time. ((a): 2 h, (b): 5 h, (c): 8 h).

Table 4. Oxygen contents (wt%) versus annealing time in AlN substrates (4 wt% YF_3) sintered at 1850°C

Dwell time (h)	O (total)	O(II)	O(III)
1	1.55	1.33	0.22
2	1.53	1.48	0.05
3	1.15	1.11	0.04
4	1.31	1.29	0.02
5	1.23	1.16	0.07
6	1.32	1.29	0.03
8	1.28	1.18	0.01

are polygonal and their size increases from $3\text{--}5\ \mu\text{m}$ to $5\text{--}8\ \mu\text{m}$. However, when the annealing time exceeds 3 h, the aluminate phase is around the AlN grains (Fig. 4(b) and (c)). Moreover, The oxygen analyses reported in Table 4 show the stability of the different oxygen contents (OII and OIII) whereas they decrease in the range 1–3 h. The thermal conductivities measured on all samples are stable whatever the dwell time (Fig. 5).

4 Discussion

The study of the influence of the additive contents, revealed that, at first, the total oxygen content increased with the YF_3 percentages, it allows the conclusion that an external oxygen reacts and is absorbed by samples. One hypothesis may be expressed: the processing of slurries may be responsible for the oxygen absorption since organic additives contain water (about 1 wt%), and the mixing is realised under air, or YF_3 like an hygroscopic product is likely to absorb up to 5% oxygen in its lattice without any phase modification.^{19,20} However, the presence of YF_3 as additive allows the decrease of the intra-granular oxygen content (0.2% OIII for 1 wt% YF_3 and 0.05% from 5 wt% OIII to 10 wt% YF_3). In fact, a diffusion process of the oxygen intragranular occurs towards the aluminate phases in the grain boundary. Some high thermal conductivities ($160\text{--}200\ \text{W m}^{-1}\ \text{K}^{-1}$) are measured with a low total oxygen content (1%), so the oxygen is not the limiting factor. On the contrary, the S.E.M. observations indicate how important is the precise location of the location of

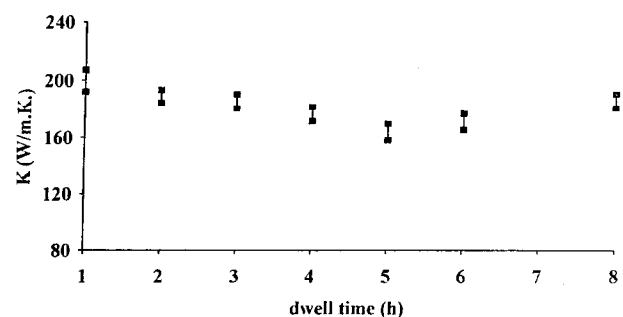


Fig. 5. Thermal conductivity versus annealing time in AlN ceramic sintered at 1850°C , 4 wt% YF_3 .

the second phases. The highest thermal conductivities are obtained with aluminate phases located at the triple points (with 4 wt% YF_3).

The study of the relationship between thermal conductivity and annealing time shows that the conductivities are higher when the AlN grain size is about 3–5 μm . Thus, the secondary phase is located at the triple points and on the edges. The decrease of the conductivity is noticed when it surrounds the grains.

5 Conclusion

The thermal conductivity improvement of $210 \text{ W m}^{-1} \text{ K}^{-1}$ is obtained with tapes containing 4 wt% YF_3 and sintered at 1850°C with a dwell time of 1 h. Thus, the intragranular oxygen content is at a minimum since the greatest part is transferred to the secondary phase. This last is poor in aluminium (formation of some YAP or YAM) and is located at the triple points or in the form of a cord along the grain edges. If the aluminate phase surrounds the grains, the thermal conductivity will decrease because of the formation of a thermal barrier between the grains. So, we can conclude that oxygen content is not a limiting factor.

We have shown that it is possible to produce some AlN substrates with yttrium fluoride as additive instead of Y_2O_3 (the use of YF_3 requires a lower weight percentage than Y_2O_3). It allows direct access to the liquid phase (YAP and/or YAM), richer in yttrium without producing any YAG phases. We have also stated the significance of the secondary phase and especially its place in the microstructure because it is responsible for the propagation or the modification of the heat flow.

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