Journal of the European Ceramic Society **11** (1993) 359–362

Evolution of the Secondary Phase AlON in AlN during its Bonding with CaO-Doped Tungsten

Paule Denoirjean-Deriu & Pierre Lefort

Laboratoire de Céramiques Nouvelles, CNRS URA 320, Faculté des Sciences, 123, Avenue Albert Thomas, 87 060 Limoges Cédex, France

(Received 11 May 1992; revised version received 26 June 1992; accepted 15 July 1992)

Abstract

The reaction of AlON with CaO, which occurs during the direct bonding between AlN ceramics and CaO-doped tungsten, induces between 1400°C and 1650°C a fast demixing of oxynitride, proceeding with a reaction between the so-formed alumina and lime, producing calcium aluminates. Their compositions are those expected on the basis of the pseudo-binary phase diagrams of AlON (for the equivalent quantity of Al_2O_3 *contained in the oxynitride) and* Al_2O_3/CaO *(for the nature of the aluminates). The aluminium nitride produced by the demixing remains after the reaction, except at the highest temperatures and CaO contents where it is dissolved by the calcium aluminate liquid phase to form a nitrogen glass. This overall behaviour is good for maintaining the properties of AlN ceramics after bonding with metal.*

Beim Diffusionsschweißen von AlN-Keramik mit CaO-dotiertem Wolfram löst die Reaktion von AlON mit CaO zwischen 1400°C und 1650°C eine schnelle Entmischung des Oxynitrids aus, die von einer Reaktion zwischen dem gebildeten Al_2O_3 *und CaO zu Calciumaluminaten gefolgt wird. Die Zusammensetzungen entsprechen den auf der Basis der pseudobinären Phasendiagramme von AlON (für die äquivalente Menge* Al_2O_3 *im Oxynitrid) und von* Al_2O_3/CaO *(für die Aluminate) zu Erwartenden. Das bei der Entmischung gebildete AlN bleibt bis zu höchsten Temperaturen und CaO-Gehalten stabil bevor es sich in der Flüssigphase aus Calciumaluminat löst und ein nitridisches Glas bildet. Das beschriebene Verfahren wirkt sich auf die Erhaltung der Eigenschaften von AlN-Keramiken nach der Fügung mit Metall positiv aus.*

La réaction de l'oxynitrure d'aluminium AlON avec CaO qui se produit pour établir la jonction entre des pièces céramiques en nitrure d'aluminium et du tungstène dopé à la chaux entraîne, entre 1400°C et 1650°C, une rapide démixion de l'oxynitrure, accompagnée d'une réaction de l'alumine ainsi formée avec la chaux pour donner des aluminates de calcium. Leurs compositions sont celles attendues en considérant d'une part le diagramme pseudo-binaire de l'oxynitrure d'aluminium (pour déterminer la quantité équivalente d'alumine contenue dans l'oxynitrure) et d'autre part le diagramme Al_2O_3/CaO *(pour fixer la nature des aluminates). Le nitrure d'aluminium produit par la démixion de l'oxynitrure subsiste après la réaction, sauf aux températures et teneurs en chaux les plus élevées où il est dissous par la phase liquide aluminate de calcium pour former un verre azoté. Ce comportement global est favorable au maintien des qualités du nitrure d'aluminium après sa liaison avec un métal.*

1 Introduction

Quériaud *et al.* have recently shown an original method[1,2] of obtaining the adhesion of metals such as tungsten on aluminium nitride by using calcium oxide as an additive in the metal. The bonding is achieved by the formation of a liquid phase of variable composition in the pseudo-binary system CaO/Al_2O_3. This secondary phase appears at the ceramic/metal interface and migrates into the metal (growing rich in calcium) and through the aluminium nitride, using the grain boundaries (with an increase of the aluminium ratio).

This bonding method is of interest for obtaining a new generation of electronic substrates with high heat dissipation. For this reason, it is very important to make sure that the thermal conductivity is not too strongly lowered by the calcium centripetal diffusion. It is well known, indeed,[3] that the thermal conductivity of aluminium nitride depends on the quantity of secondary phase located at the grain boundaries.

In the case of 'pure' aluminium nitride, the grains

Journal of the European Ceramic Society 0955-2219/93/$6.00 © 1993 Elsevier Science Publishers Ltd, England. Printed in Great Britain

are always surrounded by small amounts of amorphous alumina, giving an AlON secondary phase by heating beyond 1600°C (during its sintering).[4] Though the bonding treatment necessitates temperatures not higher than 1500°C, the preliminary sintering of the nitride, always beyond 1600°C, produces aluminium oxynitride. This AlON phase contacts the calcium oxide at the beginning of the bonding reaction, producing a calcium aluminate. Later on the calcium migrates through the AlON phase at the grain boundaries, by means of cation vacancies of AlON.

This diffusion process is not well understood, but is important, because any change of the secondary phase of the aluminium nitride may induce important modifications of the characteristics of the nitride. As no information is available concerning the reaction between AlON and CaO, its investigation is the aim of the present study.

2 Experimental

The authors have synthesized aluminium oxynitride by the route of carbothermal reduction of alumina in a nitrogen atmosphere[5] with an equivalent ratio of 28 mol% AlN. According to the AlN/Al_2O_3 phase diagram,[6] this composition is situated in the middle of the stability range of the AlON phase (Fig. 1). The equation of the reaction is:

$$0{\cdot}86Al_2O_3 + 0{\cdot}42C + 0{\cdot}14N_2$$
$$\xrightarrow{1600\ C,\ 3\,h} 0{\cdot}72Al_2O_3 + 0{\cdot}28AlN + 0{\cdot}42CO$$
$$\xrightarrow{1850\ C,3\,h} Al_{1{\cdot}72}O_{2{\cdot}16}N_{0{\cdot}28} + 0{\cdot}42CO$$

Alumina (alpha variety, diameter = 0·3 μm) was provided by Fluka A.G. (Switzerland) and contained less than 100 ppm of total impurities. Carbon is flame black from Prolabo S.A. (France) with an ash ratio lower than 1 wt%. After mixing, the powders were put in a vitreous carbon crucible, in the middle of a furnace with a graphite resistor in flowing N_2.

After reaction, the X-ray diffraction pattern did not show any impurity and the white colour of the oxynitride was another proof of its purity.[5] A light sintering occurring during the last thermal treatment necessitated a soft grinding in an agate mortar. The mixing with 20–60 wt% of lime (calcium carbonate from Prolabo S.A., calcined at 1000°C for 2 h, diameter < 1 μm and purity 99·5%) was made in the same mortar. Cylindrical specimens (diameter = 17 mm, height = 5·5 mm) were produced from these mixed powders by uniaxial compaction with 140 MPa pressure, and then put on a graphite support in the middle of the furnace already described, with N_2 flowing. The treatment lasted from 1 to 4 h, with temperatures varying between 1400 and 1650°C. After cooling, the samples were cut, ground and then analysed by X-ray diffraction. The nitrogen content was determined in a Carlo-Erba elemental analyser.

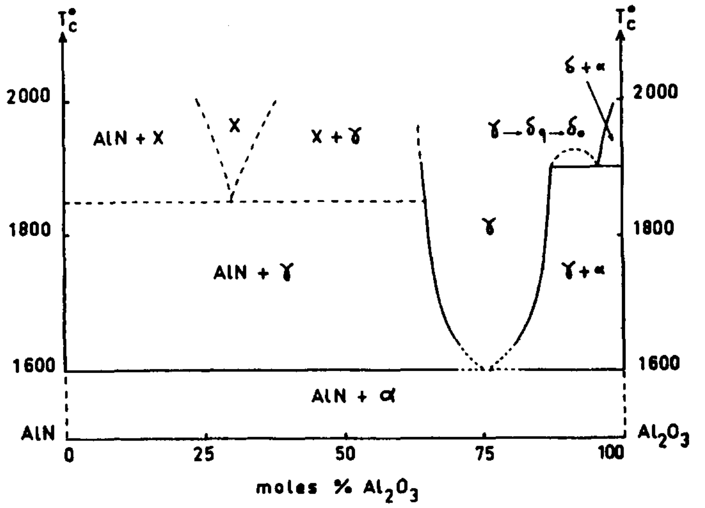

Fig. 1. AlN/Al_2O_3 phase diagram.[6]

3 Results

Regardless of the temperature or the duration, the AlON phase almost always disappeared; except in some cases in which a glassy phase was obtained, aluminium nitride and various calcium aluminates were identified by X-ray analysis. No significant loss of nitrogen was observed. The SEM observation, EDX analysis and X-ray diffraction of cross-sections showed that the aluminium nitride was generally present as dark precipitates of small size (diameter ≃ 5 μm) in the aluminate matrix, as illustrated in Fig. 2.

3.1 Influence of time

The duration of the thermal treatment had no influence on the nature of the final products, except

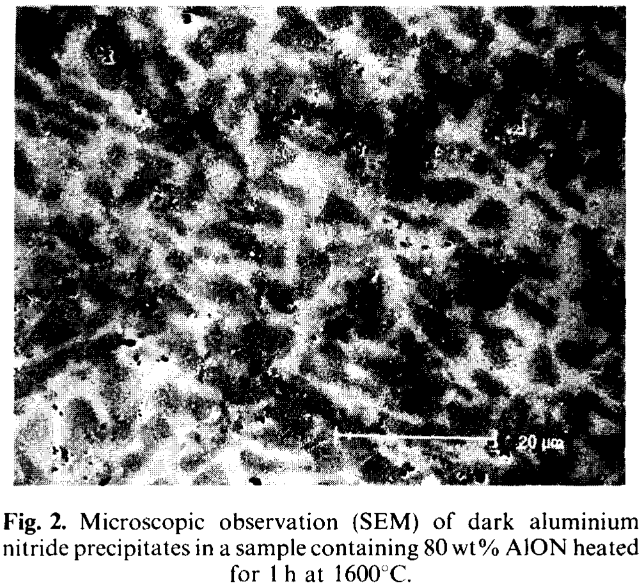

Fig. 2. Microscopic observation (SEM) of dark aluminium nitride precipitates in a sample containing 80 wt% AlON heated for 1 h at 1600°C.

Table 1. Composition of calcium aluminates versus the treatment temperature and the AlON content

wt% AlON	*40*	*50*	*60*	*80*
1400°C	$C_{12}A_7 + C_3A$	$C_{12}A_7 + C_3A$	$C_{12}A_7$ + CA + Phase X	CA_2 + CA
1500°C	$C_{12}A_7 + C_3A$	$C_{12}A_7 + C_3A$	$C_{12}A_7$ + CA + Phase X	CA_2 + CA
1600°C	C_3A	$C_{12}A_7 + C_3A$	C_3A + CA + Phase X	CA_2 + CA
1650°C	Nitrogen glass	C_3A	C_3A + CA + Phase X	CA_2 + CA

when a mixture of 80 wt% AlON and 20 wt% CaO was heated at lower temperature and for the shortest time (1400°C, 1 h). In this case, a small amount of residual AlON was found. This result proves that under experimental conditions of metal bonding on aluminium nitride,[2] the formation of fusible calcium aluminates inside the nitride is very rapid, explaining why the bonding is so easily achieved.

3.2 Influence of temperature and composition

For different mixtures and temperatures, Table 1 summarizes the different calcium aluminate phases found by X-ray analysis after 1 h of thermal treatment.

Temperature had no influence on the final products for the mixture containing 20 wt% CaO. In this case, the calcium aluminates observed were the richest in aluminium, i.e. CA_2 and CA.

As expected, when the lime content reached 40 wt%, the calcium aluminates formed were richer in calcium: $C_{12}A_7$ and CA at 1400–1500°C, C_3A and CA at 1600–1650°C. Also, in every case, some unidentified X-ray diffraction weak peaks (phase X) were observed.

For the mixtures with high percentages of lime (50–60 wt%), the C_3A aluminate and some remaining CaO were always found. At the lowest temperatures, there was also $C_{12}A_7$, and at the highest ones there appeared important quantities of nitrogen glasses containing 2·7–5·5 wt% nitrogen, and aluminium nitride was no longer identified.

4 Discussion

While no demixing of metastable AlON was ever observed when heating powders at temperatures lower than 1600°C, the systematic and rapid formation of AlN, observed here, shows that the reaction with lime brings about the demixing of aluminium oxynitride (Fig. 1).

The corresponding quantities of alumina react with lime to produce calcium aluminates. This reaction is probably simultaneous with the demixing of AlON because no trace of any alumina was detected, even when the reaction was slow and when non-reacted AlON remained.

Accordingly, Fig. 3, which represents the pseudo-binary Al_2O_3/CaO phase diagram, has a scale showing the equivalent quantities of Al_2O_3 introduced into the AlON/CaO mixtures, assuming that $AlON = 0{\cdot}72Al_2O_3 + 0{\cdot}28AlN$. The fit with the experimental result is excellent: for the mixtures containing 80 wt% AlON, the two expected phases CA and CA_2 were obtained and, when the quantity of CaO in the mixtures was increased, the expected aluminates $C_{12}A_7$ and C_3A were identified, after reaction. However, $C_{12}A_7$ is present even for the mixtures having contained 40–50 wt% AlON up to 1500°C: it shows that $C_{12}A_7$ is probably formed first or at least earlier than the other aluminates, and then reacts more slowly (non-reacted CaO was found with $C_{12}A_7$ in the mixtures with 40 wt% AlON treated at the lowest temperatures).

For the highest temperatures and contents of lime, the formation of a nitrogen glass agrees with previous published results concerning the Ca–Al–O–N system;[7] it was established there that, at 1700°C, the nitrogen glass formation is achieved by dissolution of AlN in liquid calcium aluminate after 15 min. In the present case, the temperature being lower, a few traces of C_3A were found.

So, the main result of this study is to prove that the overall behaviour of the secondary phase AlON is the same as the one of a mixture of Al_2O_3 and AlN, even at the temperature where the oxynitride is stable, beyond 1600°C. From this, it is not surprising that global results in good agreement with previous work about the phase relationships in the system

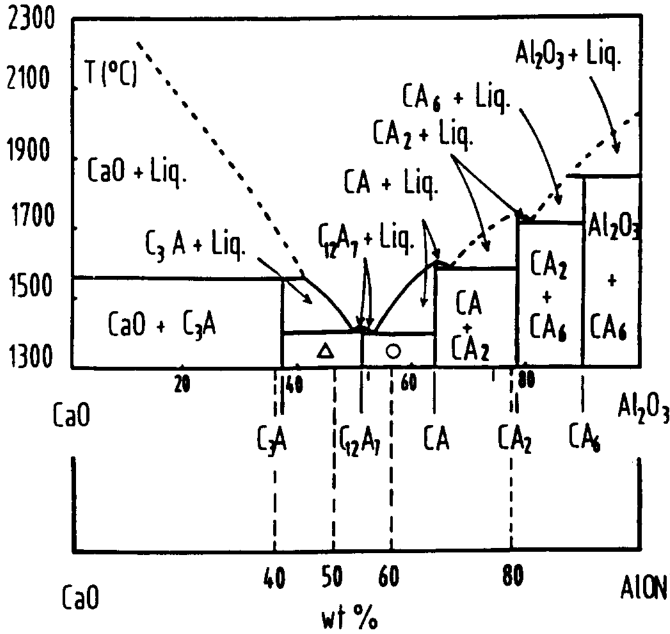

Fig. 3. Pseudo-binary Al_2O_3/CaO phase diagram. ○, $C_{12}A_7$ + CA; △, $C_{12}A_7 + C_3A$.

Ca–Al–O–N or about direct mixing of AlN with Al_2O_3 and CaO[7,8] are obtained: considering the oxynitride as a mixture of Al_2O_3 and AlN and adding CaO, the resulting phases are the same as when the aluminium nitride is added to the different phases of the Al_2O_3/CaO system.

5 Conclusion

The reaction of aluminium oxynitride with lime is a very interesting practical result for the bonding of metals such as tungsten to aluminium nitride: because of the demixing of AlON into AlN and Al_2O_3, the overall volume of the secondary phase at the grain boundaries of the nitride may be only slightly increased when the produced aluminate has a low calcium content. For instance, the volumic ratio of CA_2 to AlON (the most probable phase inside the nitride) is 1·35. This explains why no appreciable modification in the thermal diffusion of tungsten screen-printed AlN substrates was observed.[9] So, it can be expected that, by using aluminium nitride with a low oxygen content as an electronic substrate, the bonding process with CaO additive in the metal[1,2] does not affect the thermal conductivity of the substrate.

References

1. Quériaud, R., Lefort, P. & Billy, M., Compatibility between tungsten and aluminium nitride. In *Proceedings of the 1st European Conference on Advanced Materials and Process, Euromat 89*, Vol. 2, ed. H. E. Exner. DGM, Oberursel, 1990, p. 903.
2. Quériaud, R., Lefort, P. & Billy, M., The direct bonding between AlN ceramics and CaO-doped tungsten. *J. Eur. Ceram. Soc.*, **8** (1991) 319.
3. Slack, G. A., Nonmetallic crystals with high thermal conductivity. *J. Phys. Chem. Solids*, **34** (1973) 321.
4. Ado, G., Bernache, D., Billy, M., Han, K. S. & Lefort, P., Mécanisme de frittage sous charge du nitrure d'aluminium et de l'oxynitrure AlON. *Rev. Chimie Minérale*, **22** (1985) 473.
5. Guillo, P., Thesis, Une céramique polycrystalline transparente: l'oxynitrure d'aluminium gamma, propriétés mécaniques et optiques. Université de Limoges, 1985, No. 32-85.
6. Lejus, A. M., Sur la formation à haute température de spinelles non stoechiométriques et de phases dérivées dans plusieurs systèmes d'oxydes à base d'alumine et dans le système alumine–nitrure d'aluminium. *Rev. Int. Hautes Temp. et Réfract. Fr.*, **1** (1964) 53.
7. Doradoux, C., Jarrige, J. & Billy, M., Sur l'existence de verres azotés dans le système Ca–Al–O–N. In *Proceedings of Science of Ceramics 13, J. de Phys.*, **47** (1986) C1–479.
8. Schuster, J. C., Phase diagrams relevant for sintering aluminium nitride based ceramics. *Rev. Chimie Minérale*, **24** (1987) 676.
9. Quériaud, R., Thesis, Conditions d'adhésion des métaux réfractaires (W et Mo) au nitrure d'aluminium; application aux substrats cofrittés pour l'électronique. Université de Limoges, 1991, No. 11-91.