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A New Method for Fabrication of Dense Aluminium Nitride Bodies at Temperatures as Low as 1600°C

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Abstract

The sintering behaviour of aluminium nitride in the presence of yttrium oxide associated with calcium aluminate (12CaO . 7Al$_2$O$_3$) or calcium yttrium aluminate (CaYAlO$_4$) was studied in this work. The use of these compositions as additives permits significant lowering of the sintering temperature. It leads to dense bodies at temperatures less than 1600°C. The aluminate phases result in the formation of a liquid phase at low temperatures but the composition of this liquid evolves rapidly to more refractory phases in the presence of alumina contained in the AlN powder. The yttrium oxide retards the change of the liquid composition by increasing the liquid viscosity and displacing its composition to calcium yttrium aluminate phases. 97% of the theoretical density can be obtained by sintering AlN at 1600°C for 30 min with 2 wt% as total content additive. The secondary phases formed are the refractory aluminates CaO . 2Al$_2$O$_3$, CaO . Al$_2$O$_3$ and CaYAl$_3$O$_7$.

Die Sinterung von AlN im Beisein von Yttriumoxid und 12CaO . 7Al$_2$O$_3$ oder CaYAlO$_4$ ermöglicht eine Verringerung der Verdichtungstemperatur. Es können dichte Sinterkörper bei 1600°C erreicht werden. Die bei niedrigen Sintertemperaturen entstehenden Aluminatphasen führen zur Bildung einer flüssigen Phase bei niedriger Temperatur, wobei die mit Al$_2$O$_3$ reagierende Schmelze ihre Zusammensetzung in Richtung höherer Schmelztemperaturen verändert. Durch Erhöhung der Schmelzviskosität verhindert das anwesende Yttriumoxid die Veränderung der Schmelze in die Richtung einer Kalzium–Yttrium-aluminat–Zusammensetzung. 97% der theoretischen Dichte können durch Sinterung von AlN mit 2 Gew.% Additiv bei 1600°C in 30 Minuten auf diese Weise erreicht werden. Die sich bildenden Sekundärphasen sind die hochschmelzenden Verbindungen CaO . 2Al$_2$O$_3$, CaO . Al$_2$O$_3$ und CaYAl$_3$O$_7$.

Le frittage du nitrure d'aluminium en présence d'oxyde d'yttrium associé à l'aluminate de calcium (12CaO . 7Al$_2$O$_3$) ou à l'aluminate double de calcium et d'yttrium CaYAlO$_4$ permet d'abaisser la température. Il conduit à des pièces denses à 1600°C. Les phases secondaires aluminates apparaissant pendant le frittage résultent de la formation d'une phase liquide à basse température, mais la composition de ce liquide dérive rapidement vers des compositions plus réfractaires grâce à la présence de l'alumine contenu dans la poudre de nitrure d'aluminium. L'oxyde d'yttrium retarde l'évolution de la composition de la phase liquide en augmentant sa viscosité et en déplaçant sa composition vers des phases aluminates de calcium. A 1600°C pendant 30 minutes, il est possible de densifier le nitrure d'aluminium à 97% avec seulement 2% en masse d'ajouts. Les phases secondaires sont constituées des aluminates CaO . 2Al$_2$O$_3$, CaO . Al$_2$O$_3$ et CaYAl$_3$O$_7$.

1 Introduction

Like all other nitride materials, the preparation of a dense AlN body requires the presence of a liquid phase which facilitates mass diffusion. Usually the liquid phase is obtained by using alkaline earth or rare earth oxides.[1–6] However, the high temperatures used make its fabrication, as a substrate in microelectronics, expensive. For this reason, several studies were carried out to reduce these temperatures, using a mixture of oxides as sintering additives.[7–8] Troczynski & Nicholson[8] obtained a dense material by heating AlN at 1600°C for 1 h with a mixed additive of Y$_2$O$_3$, CaO, La$_2$O$_3$, CeO$_2$ and SiO$_2$. However, the amount of additive used was very high: 9 wt%. Streicher *et al.*[9] sintered AlN at 1650°C in the presence of 0.5 wt% of CaCO$_3$ or 3CaO . 3SiO$_2$. Al$_2$O$_3$. In the present case, AlN has been successfully densified at 1600°C

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with a mixture of CaO and 12 CaO . 7 Al_2O_3 (abbreviated $C_{12}A_7$).[10]

It is well known that materials sintered with a Y_2O_3 additive have better mechanical properties at high temperature than materials containing CaO. This motivated the choice of Y_2O_3, $C_{12}A_7$ or $CaYAlO_4$ as additives for sintering with the additional advantage of liquid phase formation at low temperature. For comparison, AlN was sintered with a CaO and Y_2O_3 mixture.

2 Experimental Procedure

The starting AlN material consisted of submicronic agglomerates produced by Koch-Light. The neutron activation analysis[11] indicated 3 wt% oxygen. A grain size of less than 10 μm was obtained by sieving in petroleum ether.

The aluminates were prepared by milling and mixing Al_2O_3 and CaO or Y_2O_3, by pressing, and then firing at 1300°C for 2 h in air. After the reaction, samples were crushed and ground in an agate mortar. CaO was obtained by calcination of $CaCO_3$ at 1000°C. Table 1 gives the characteristics of the starting powders.

Table 1. Characteristics of starting powders

Products	*Origin*	*Purity*	*Size (μm)*
$CaCO_3$	Merck	99·9	5·0
α-Al_2O_3	Alcoa	99·9	0·4
Y_2O_3	Rhône Poulenc	99·9	0·4

The AlN powder was blended with additives in an agate mortar and then homogenized for 1 h in a mixer. After mixing, the powder mixtures were uniaxially pressed into pellets at 200 MPa. Green density reached 60% of the theoretical density. Before being sintered in a dry N_2 gas flowing furnace, the samples were covered with AlN powder in a graphite crucible in order to limit its decomposition.[12]

The density of the sintered material was measured using Archimede's technique. The obtained products were examined with a scanning electron microscope and analysed by X-ray diffraction.

Results and Discussion

3.1 Sintering of AlN with CaO–Y_2O_3 mixtures

AlN was sintered at 1700°C for 30 min with additive amounts between 2 and 10 wt%. Table 2 summarizes the results. It is noted that, independently of the total additive content, the highest density is obtained, as observed by Michelet,[13] in the presence of equal weight quantities of CaO and Y_2O_3. Morever, the results show that CaO–Y_2O_3 mixtures promote densification more than CaO or Y_2O_3 when used separately. Finally, as shown in Fig. 1, the relative density reaches its maximum for a weight ratio of CaO : Y_2O_3 = 1 and a total sintering aid content equal to 2 wt%.

Table 2. Relative density of AlN sintered at 1700°C for 1 h with CaO–Y_2O_3 mixture

CaO (wt%)	*Total additive contents (wt%) Y_2O_3 + CaO*				
	2	4	6	8	10
0	86	81	70	70	70
0·5	94	88			
1	97	92	81	80	80
1·5	96	94			
2	92	96	88	87	86
2·5		95			
3		94	91	89	89
3·5		92			
4		88	89	90	90
5			88	89	91
6			85	88	90
7				87	89·5
8				84	88
9					86
10					84

SEM micrographs of the fracture surfaces of three samples sintered with 2 wt% of various additives show a distinct difference in the microstructure of materials (Fig. 2). Figure 2(a) shows that the grains of specimens heated with only Y_2O_3 present a small facet, of the order of 1 μm. As shown in Fig. 2(b) and (c), the addition of CaO or CaO–Y_2O_3 enhances densification. The liquid thus formed leads to a rounded grain shape and grain growth. For specimens sintered with CaO–Y_2O_3, X-ray diffraction analysis shows that the crystalline phases formed are similar to those of the systems CaO–Al_2O_3[14] and CaO–Y_2O_3–Al_2O_3.[15] The aluminate phases CA_2(CaO . 2Al_2O_3), CA(CaO . Al_2O_3) and $CaAlYO_4$ are identified.

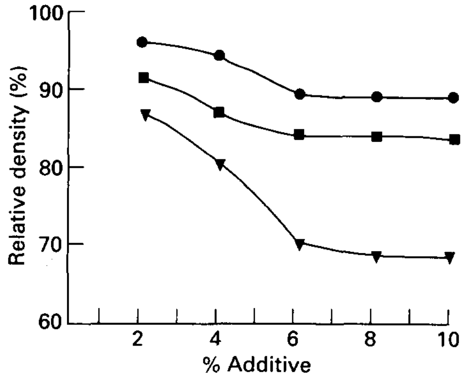

Fig. 1. Evolution of the relative density of samples sintered at 1700°C for 30 min with additive contents. ●, CaO–Y_2O_3; ■, CaO; ▼, Y_2O_3.

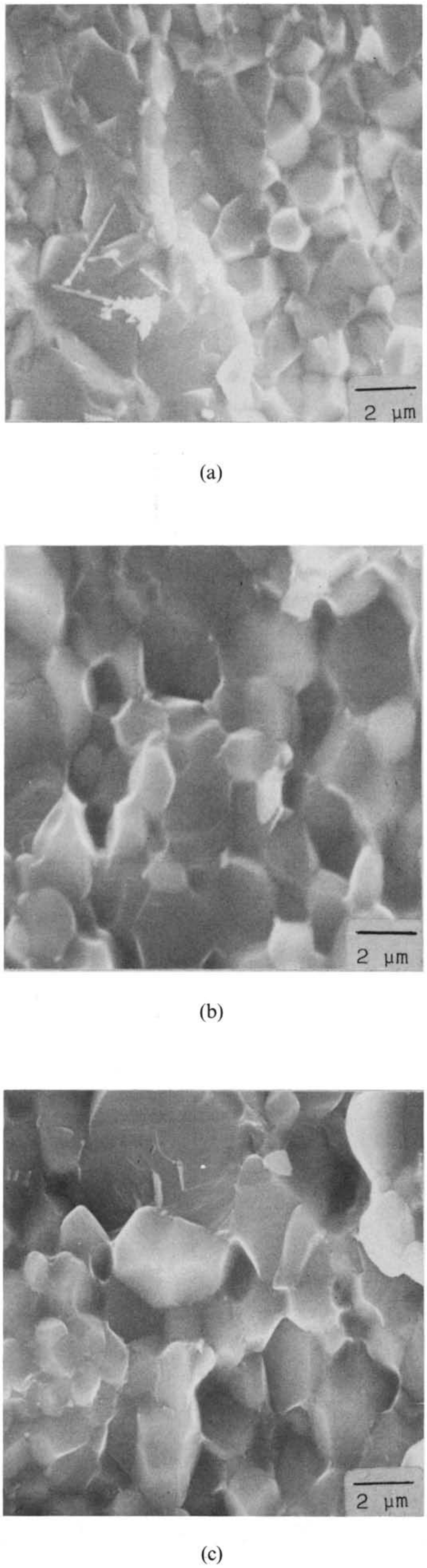

Fig. 2. SEM micrographs of samples sintered at 1700°C with various additives. (a) AlN + 2 wt% Y_2O_3; (b) AlN + 1 wt% Y_2O_3 + 1 wt% CaO; (c) AlN + 2 wt% CaO.

At 1700°C, the phase diagram of the Al_2O_3–CaO binary system indicates the formation of calcium aluminate liquid, which normally promotes densification. However, the Al_2O_3 contained in the AlN powder enriches the liquid in alumina driving a rapid evolution to the formation of refractory aluminates. The addition of yttrium oxide increases the liquid viscosity and limits the observed change of composition to the refractory phases by displacing the composition of the secondary phases to those of calcium yttrium aluminates which are given in Fig. 3. Y_2O_3 also maintains the liquid phase for a longer time, yielding a better densification of the material.

3.2 Sintering of AlN with Y_2O_3–12 CaO . 7 Al_2O_3 mixtures

Three series of samples were sintered at 1700°C for 30 min with the total additive contents 2, 4 and 6 wt% respectively. For each sample, various weight ratios $Y_2O_3 : CaO : C_{12}A_7$ were used.

Relative density versus sintering additives, weight losses and secondary phases formed are given in Table 3. From these results two observations can be made. Firstly for each series the green bodies prepared with the mixtures Y_2O_3–$C_{12}A_7$ are more dense. Secondly the density maximum is recorded with the lowest additive amount ($Y_2O_3 = C_{12}A_7 = 1\%$). The X-ray diffraction reveals that the secondary phases formed are similar to those obtained with Y_2O_3–CaO. The observed weight losses, which are responsible for the decrease in the relative density, are essentially due to the penetration of the liquid phase through the powder bed. However, the volatilization of calcium at this temperature is not excluded and may contribute to weight loss.[1]

Figure 4 shows that the relative density increases very rapidly from 1550°C to 1600°C and then continues increasing slightly. At 1600°C, the density reaches 96% of the theoretical density after 30 minutes of heat treatment. The low density (82%) observed at 1550°C can be explained by the low quantity of the liquid phase formed. Increasing the additive content or the sintering time would normally result in an increase in density. A specimen heated during 2 h has a relative density greater than 90%.

The influence of the temperature was studied in the range varying from 1550 to 1700°C using the composition which leads to optimum densification (1% $C_{12}A_7$–1% Y_2O_3). Densities versus sintering time at 1600°C are shown in Fig. 5. At this temperature the enhanced densification may be due to the increase in liquid amount. For example, the relative density reaches 93% after only 5 min of heat treatment and 97% after 1 h. The micro-

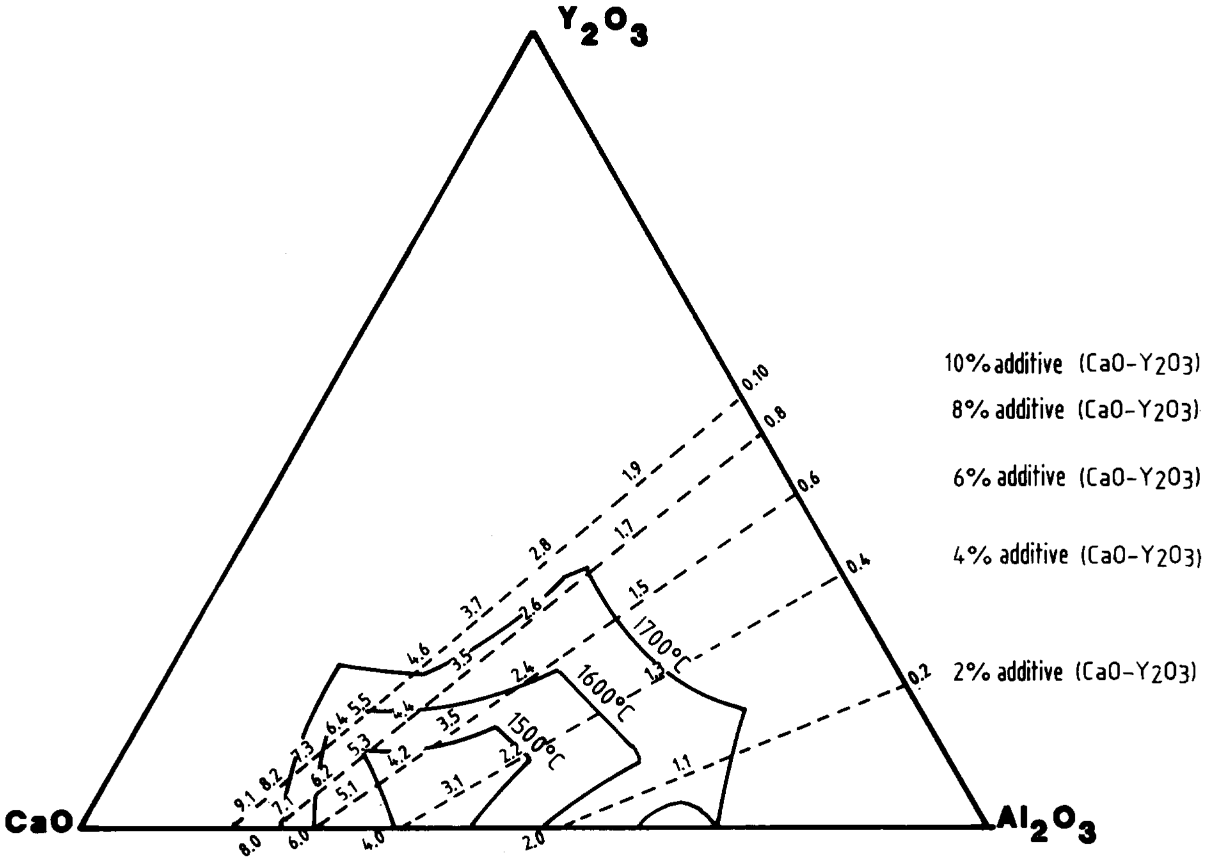

Fig. 3. Evolution of the secondary phases nature with additive contents.

graphs in Fig. 6 confirm this evolution. Figure 6(a), which refers to the initial stage, shows significant intergranular porosity subsequently eliminated with grain growth, when sintering time is increased (Fig. 6(b), 6(c)). X-Ray diffraction measurements reveal the presence of the calcium aluminates CA_2 and CA, and the dialuminate $CaYAl_3O_7$.

Under these conditions, the densification of AlN with Y_2O_3–$C_{12}A_7$ as sintering additives is similar to its densification in the presence of the liquid phase. The yttrium oxide is used as an additional element to limit the composition change of the liquid to refractory phases. This occurs by displacing the composition of secondary phases to the centre of the Al_2O_3–CaO–Y_2O_3 ternary diagram, where the vitreous domains are larger.[10] In this manner, the liquid phase is conserved longer during sintering. Therefore, it seemed to us worth considering the use of $CaAlYO_4$ dialuminate as an additive.

Table 3. Relative density and weight losses of AlN sintered at 1600°C with various additives

Number	Y_2O_3	*CaO*	$Y_{12}A_7$	*d* *(%)*	$\Delta m/m_0$ *(%)*	*Crystalline phases*
1	1	1	—	95·2	3·0	CA_2–$CaAlYO_4$
2	1	—	1	97·2	2·7	CA_2–$CaAlYO_4$
3	0·5	0·5	1	96·4	2·8	CA_2–$CaAlYO_4$
4	1	0·5	0·5	96·8	3·3	CA_2–$CaAlYO_4$
5	2	2	—	95·4	3·0	CA–$CaAlYO_4$
6	2	—	2	96·2	3·0	CA_2–Ca–$CaAlYO_4$
8	2	1	1	95·9	4·4	CA_2–Ca–$CaAlYO_4$
9	3	3	—	91·7	6·6	$C_{12}A_7$–CA–$CaAlYO_4$
10	3	—	3	93·7	6·6	C_{12}A7–CA–$CaAlYO_4$
11	1·5	1·5	3	93·1	6·2	CA–$CaAlYO_4$

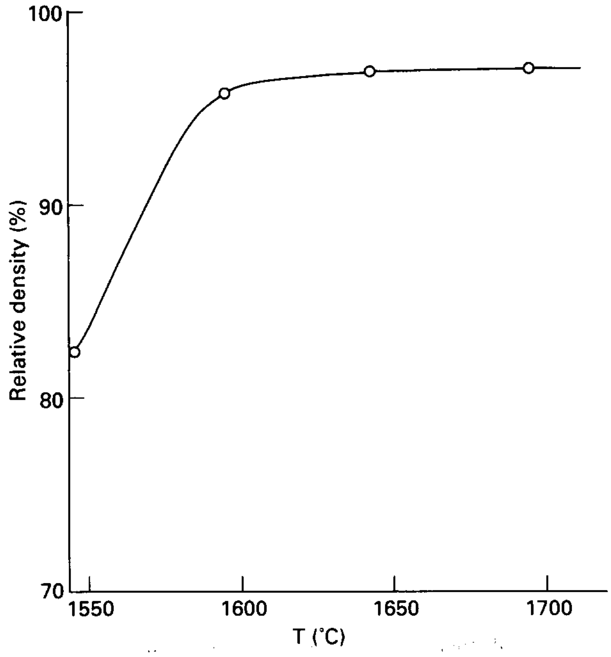

Fig. 4. Relative density versus temperature of samples sintered for 30 min with 1 wt% $C_{12}A_7$–1 wt% Y_2O_3.

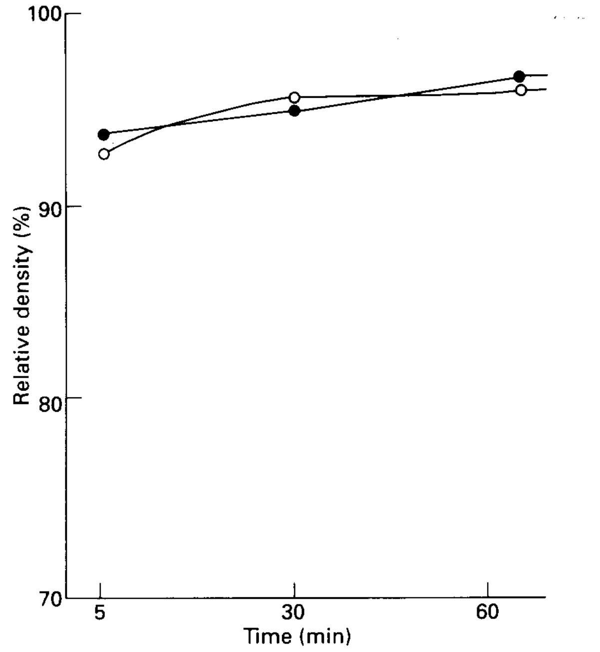

Fig. 5. Relative density versus sintering time at 1600°C. (○), 1 wt% $C_{12}A_7$–1 wt% Y_2O_3; (●), 2 wt% $C_{12}A_7$–2 wt% Y_2O_3.

3.3 Sintering of AlN with the dialuminate $CaYAlO_4$

Figure 7 summarizes results of AlN sintering at 1600 and 1650°C with various additive contents. It is noted that the relative density is a maximum for low additive contents (1 wt% at 1650°C and 2 wt% at 1600°C). The X-ray diffraction measurements (Table 4) reveal the formation of CA_6 ($CaO.6Al_2O_3$) and CA_2 phases. With increasing additive contents the relative density somewhat decreases. In this case the phases CA, $C_{12}A_7$ and $CaYAl_3O_7$ were identified. The decrease in density seems in contradiction with the secondary phases formed, which at these temperatures are liquid and would lead to dense materials. As reported,[10] these liquid aluminates have both very high viscosity and low wetting. These two properties produce an intragglomerate porosity which limits the densification.

In order to confirm this assumption, AlN was sintered at 1600°C with 1 wt% of dialuminate. Figure 8 shows that the densification increases slightly and regularly as time is increased. A sample heated for 1 h has 96% of theoretical density.

To reduce the high viscosity of the liquid phase CaO or Y_2O_3 were added to the sintering additive $CaYAlO_4$. Figure 9 shows that the addition of CaO promotes densification by leading to the formation of significant liquid phase which attenuates the low wetting of the dialuminate. However, the increasing temperature reduces this influence. For those samples sintered with

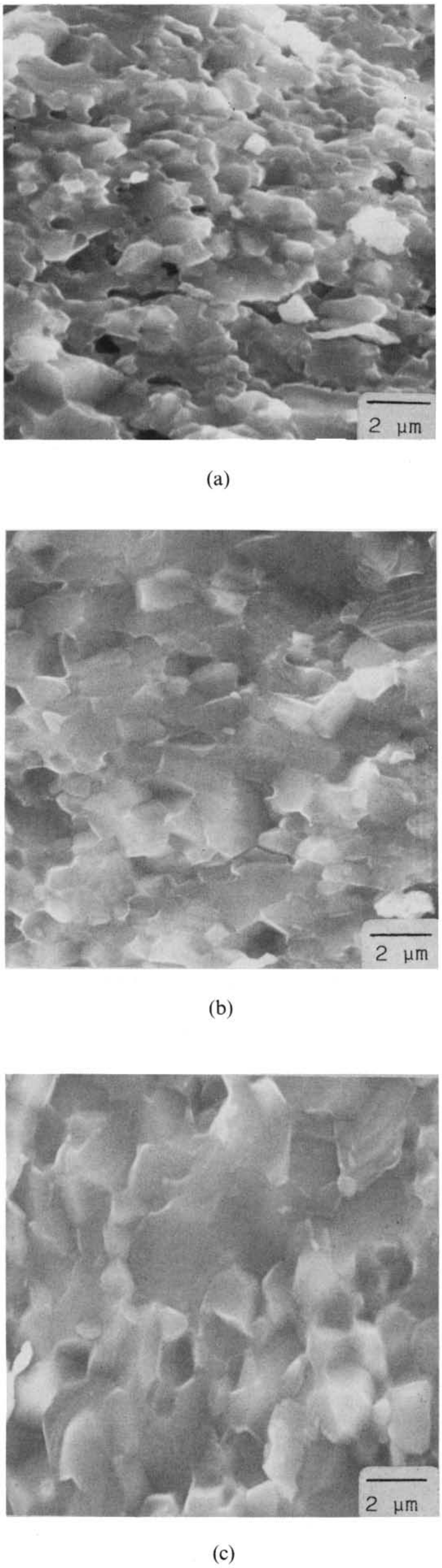

Fig. 6. SEM micrographs of samples sintered at 1600°C with 2 wt% Y_2O_3-2 wt% $C_{12}A_7$ for: (a) 5 min; (b) 30 min; (c) 60 min.

Table 4. Intergranular phases of AlN sintered for 1 h with $CaYAlO_4$ as additive

	$CaYAlO_4$ (%)					
T (°C)	*1*	*2*	*4*	*6*	*8*	*10*
1650	CA_6–CA_2	CA_6–CA_2 $CaYAl_3O_7$	CA_2–CA $CaYAl_3O_7$	CA $CaYAl_3O_7$	CA–$C_{12}A_7$ $CaYAl_3O_7$	CA–$C_{12}A_7$ $CaYAl_3O_7$
1600	CA_6–CA_2	CA_6–CA_2 $CaYAl_3O_7$	CA_2–CA $CaYAl_3O_7$	CA $CaYAl_3O_7$	CA–$C_{12}A_7$ $CaYAl_3O_7$	CA–$C_{12}A_7$ $CaYAl_3O_7$

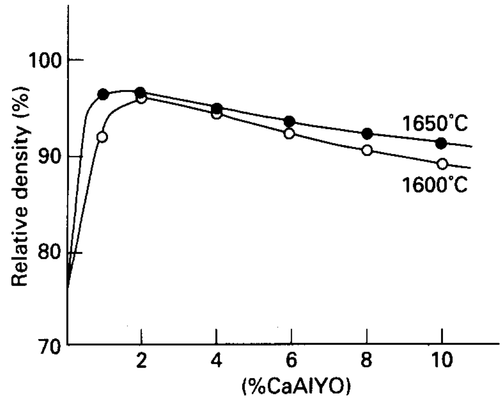

Fig. 7. Relative density versus additive contents of samples sintered at 1600 and 1650°C.

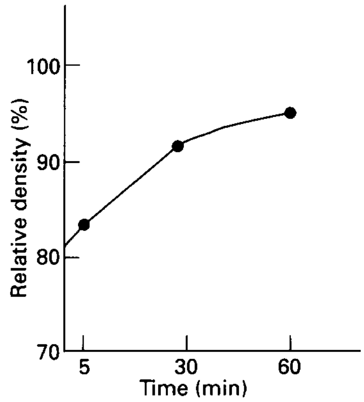

Fig. 8. Relative density versus sintering time at 1600°C with 1 wt% $CaYAlO_4$.

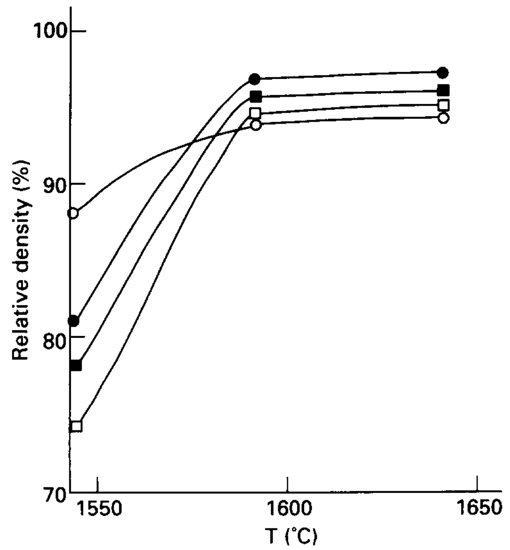

Fig. 9. Evolution of the relative density with temperature of samples sintered with $CaYAlO_4$ and CaO or Y_2O_3. (○), 1 wt% $CaYAlO_4$–1 wt% CaO; (●), 1 wt% $CaYAlO_4$–1 wt% Y_2O_3; (□), 1wt% $CaYAlO_4$; (■), 2 wt% $CaYAlO_4$.

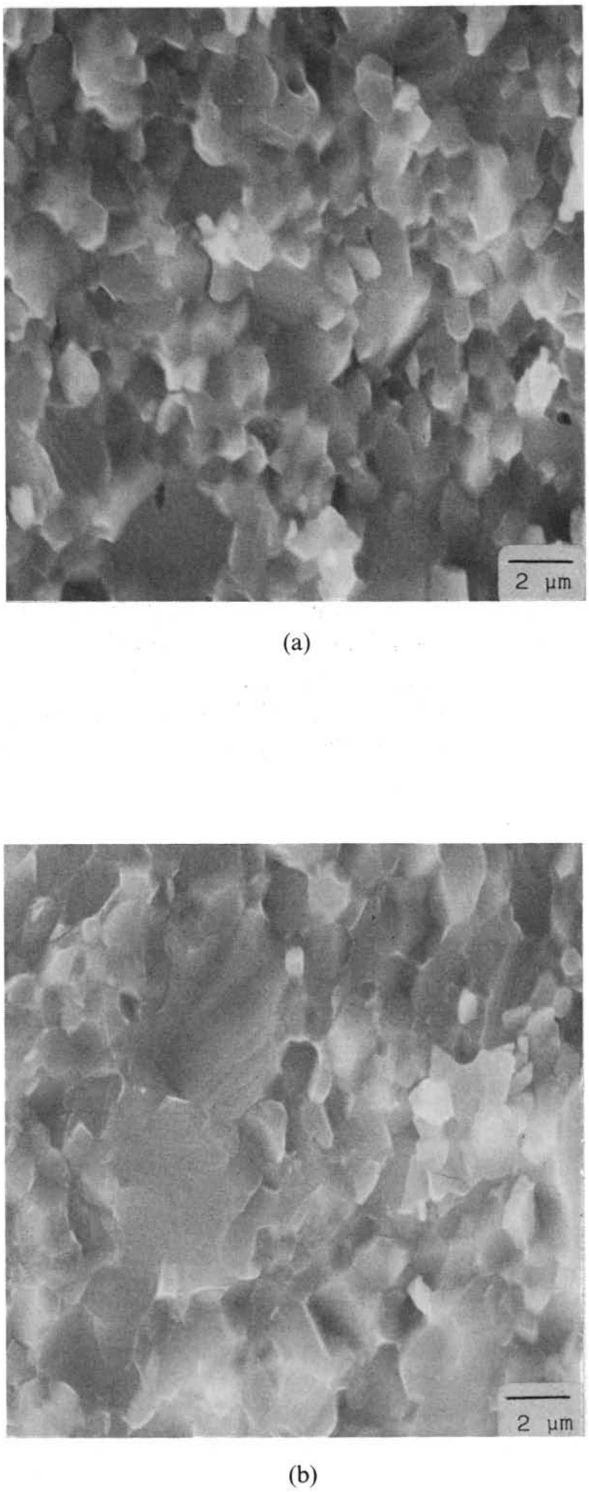

Fig. 10. SEM micrographs of samples sintered at 1650°C with: (a) 1 wt% $CaYAlO_4$; (b) 1 wt% $CaYAlO_4$–1 wt% Y_2O_3.

$CaYAlO_4$–Y_2O_3 mixtures the densification curve is similar to the one obtained with 2 wt% of $CaYAlO_4$. The micrographs of Fig. 10 show, in comparison with $CaYAlO_4$, that the $CaYAlO_4$–Y_2O_3 mixture improves densification. Y_2O_3 does not form the liquid phase but induces a change of the secondary phase composition to the centre of the phase diagram CaO–Y_2O_3–Al_2O_3, where the vitreous domain is larger. This phenomenon leads to material densification by delaying the formation of refractory aluminates.

4 Conclusion

The results of the present study demonstrate that the use of Y_2O_3–$C_{12}A_7$ or $CaYAlO_4$–$C_{12}A_7$ mixtures as sintering additives permits the densification of aluminium nitride at temperatures as moderate as 1600°C. $C_{12}A_7$ which has a low melting point leads to the formation of a liquid phase at low temperature. Y_2O_3 or $CaYAlO_4$ limits and delays the evolution of this liquid composition to refractory phases by increasing the liquid's viscosity and displacing the composition of the secondary phases to the centre of the Al_2O_3–CaO–Y_2O_3 ternary diagram. For example, the addition of 1wt% Y_2O_3–1wt% $C_{12}A_7$ or 1wt/% $CaYAlO_4$–1wt% $C_{12}A_7$ to AlN leads to dense materials (97%) after 1 h. Moreover, the secondary phases formed are similar to those for AlN sintered with CaO or Y_2O_3, which is beneficial for the mechanical properties. It will be noted that this temperature is not the lowest one at which AlN can be sintered. In the same way, 90 % of the theoretical density was obtained after 2 h by sintering AlN at 1550°C with Y_2O_3–$C_{12}A_7$. The sintering temperatures could also be reduced by using AlN powder containing less oxygen.

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