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Densification and Thermal Conductivity of Low-Sintering-Temperature AlN Materials

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Abstract

The aim of the study was the sintering of aluminium nitride at rather low temperatures (≤1650°C). Various sintering aids were studied, in particular Al-, Si- and Ca-based oxides. $CaCO_3$ *and* $3CaO–3SiO_2–Al_2O_3$ *are the most efficient additives, because quantities as low as 0·5 wt% are enough to yield sintered AlN substrates with no open porosity. TEM observations showed that low concentrations of* $CaCO_3$ *or* $CaSiO_3$ *lead to location of the secondary phases at the triple points, whereas high concentrations lead to wetting of the grains. Thermal diffusivity of sintered materials was determined by a laser flash method. The highest conductivity (70 W* m^{-1} K^{-1}*) is obtained with* $CaCO_3$ *additions. These additions promote liquid formation, which cleans the surface of the AlN grains from oxygen and thereby prevents oxygen from entering the AlN lattice. The* $CaAl_2O_4$ *compound exhibits a lower thermal conductivity than the* $CaAl_4O_7$ *and* $Ca_3Al_{10}O_{18}$ *compounds. The* $Ca_2SiAl_2O_7$ *compound and the 27R AlN polytype have a strong negative influence on the thermal conductivity of sintered materials.*

Das Ziel dieser Untersuchung war, Aluminiumnitrid bei relativ niedrigen Temperaturen (≤1650°C) zu sintern. Es wurden verschiedene Sinterhilfsmittel untersucht, speziell Al-, Si- und Ca-haltige Oxide. $CaCO_3$ *und* $3CaO–3SiO_2–Al_2O_3$ *sind die effektivsten Additive, weil auch niedrige Gehalte von 0·5 Masse-% ausreichen, um AlN-Substrate mit geschlossener Porosität herzustellen. TEM-Untersuchungen zeigen, daß niedrige* $CaCO_3$*- oder* $CaSiO_3$*-Konzentrationen zu einer zweiten Phase an den Trippelpunkten führen, wogegen hohe Konzentrationen die Körner benetzen. Die Temperaturleitfähigkeit der gesinterten Proben wurde mit der Laser flash Methode bestimmt. Die höchste Leitfähigkeit (70 W* m^{-1} K^{-1}*) wird mit dem* $CaCO_3$*-Additiv erreicht. Dieses Additiv fördert die Flüssigphasenbildung, die die Oberflächen der AlN-Körner von Sauerstoff reinigt und daher die Diffusion von Sauerstoff in das AlN-Gitter verhindert. Die* $CaAl_2O_4$*-Verbindung führt zu einer niedrigeren thermischen Wärmeleitfähigkeit als* $CaAl_4O_7$ *und* $Ca_3Al_{10}O_{18}$*-Verbindungen.* $Ca_2SiAl_2O_7$ *und die 27R AlN-Polytypen haben einen starken negativen Einfluß auf die Wärmeleitfähigkeit der gesinterten Werkstoffe.*

Le but de cette étude est le frittage du nitrure d'aluminium à basses températures (≤1650°C). Différents additifs de frittage ont été étudiés, en particulier des oxydes à base d'Al, de Si et de Ca. Le $CaCO_3$ *et le* $3CaO–3SiO_2–Al_2O_3$ *sont les plus efficaces car des quantités de 0·5% massique sont suffisantes pour donner des substrats frittés ne présentant plus de porosité ouverte. Des observations par TEM montrent que de faibles concentrations de* $CaCO_3$ *ou de* $CaSiO_3$ *entraînent une localisation des*

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phases secondaires aux points triples, alors que des concentrations élevées conduisent au mouillage des grains. La diffusivité thermique des matériaux frittés a été déterminée par la méthode de flash laser. La conductivité la plus élevée (70 $Wm^{-1}K^{-1}$) a été obtenue avec des ajouts de $CaCO_3$. Ces additions provoquent la formation d'un liquide qui extrait l'oxygène de la surface des grains, l'empêchant ainsi de pénétrer dans la maille cristalline de l'AlN. Le composé fritté à l'aide de $CaAl_2O_4$ présente une conductivité thermique plus faible que ceux contenant $CaAl_4O_7$ ou $Ca_3Al_{10}O_{18}$. Le $Ca_2SiAl_2O_7$ et le polytype 27R de l'AlN ont une influence néfaste sur la conductivité thermique des matériaux.

1 Introduction

Like silicon nitride, aluminium nitride is not easy to sinter, and three solutions are usually proposed to accelerate the densification kinetics:

(i) the use of high specific surface area AlN powders,[1-3] which promotes diffusion at the surface of grains and along the grain boundaries;
(ii) the use of hot pressing or hot isostatic pressing,[4,5] which brings an external driving energy for densification; moreover, new densification mechanisms can occur, e.g. plastic flow;
(iii) the use of sintering aids, which leads to the formation of a liquid phase; in particular, eutectics can form from reactions between AlN and the additives, or between the alumina layer at the surface of AlN grains and the additives; common sintering aids are Y_2O_3[6-8] and CaO.[9-11]

The sintering temperature of Y_2O_3–AlN products is generally ≥1750°C. This requires expensive firing equipment, which could limit the industrial development of AlN substrates. The aim of this study was to determine the conditions in which to sinter AlN materials at temperatures ≤1650°C. Calcium compounds were chosen as additives because they yield eutectics in the Al_2O_3–CaO system. This allows the formation of liquid phases at low temperatures (1400°C; see Fig. 1). The influence of the nature and quantity of sintering aids on the densification of AlN was studied, as well as the sensitivity of thermal conductivity to the location of secondary phases (segregated at the triple points or disseminated along the grain boundaries).

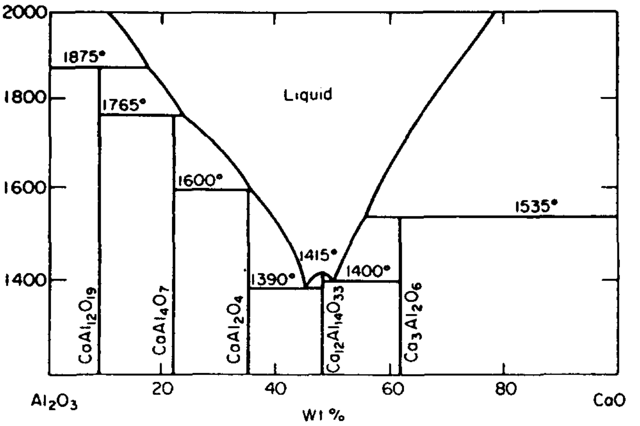

Fig. 1. Phase diagram[12] for the system Al_2O_3–CaO.

2 Experimental

2.1 Starting materials

The AlN powder used was the 'C' grade from Starck. One sintering aid was calcite ($CaCO_3$, labelled as C). Silica-based additives are reputed to be detrimental to the densification and thermal conductivity of AlN.[13,14] However, preliminary work conducted in our laboratory did not entirely support this view. Three calcium silicates were therefore also chosen, namely those of molar compositions $3CaO–3SiO_2–Al_2O_3$ (C3S3A), $CaO–2SiO_2–Al_2O_3$ (CS2A) and $CaO–SiO_2$ (CS). The aluminates were prepared by ball-milling and reactive calcination of $CaCO_3$ (Merck), SiO_2 (C800–Sifraco) and Al_2O_3 (Al6SG–AlCoA) mixtures. The compositions are given in Table 1.

2.2 Sample preparation

Samples with the shape of 10-mm diameter, 4-mm-thick disks were stamped from tape-cast specimens and then thermocompressed. The pyrolysis of organic components and the sintering treatment (at a temperature of 1650°C) were carried out by the XERAM Company (Pechiney, France).

2.3 Sample characterization

The apparent density and open porosity were measured by Archimedes's method in water. The

Table 1. Compositions studied

Materials	*Additive content (wt%)*					
C–AlN	0·5	1	1·5	2	4	6
CS–AlN	0·5	1	1·5	2	4	6
C3S3A–AlN	0·5	1	1·5	2	4	6
CS2A–AlN	—	—	—	2	4	6

Table 2. Influence of additives on density and open porosity of AlN

Materials		*Additive content (wt%)*					
		0·5	*1*	*1·5*	*2*	*4*	*6*
C–AlN	ρ (g cm^{-3})	3·22	3·20	3·19	3·17	3·05	2·84
	P_0 vol%	0·1	0·25	0·7	0·5	0·6	3
CS–AlN	ρ (g cm^{-3})	3·08	3·10	3·15	3·21	3·18	3·15
	P_0 vol%	1·5	0·5	0·3	0·3	0·1	0·3
C3S3A–AlN	ρ (g cm^{-3})	3·25	3·24	3·225	3·23	3·20	3·11
	P_0 vol%	0	0	0·1	0·1	0·4	2·5
CS2A–AlN	ρ (g cm^{-3})	—	—	—	3·13	3·24	3·23
	P_0 vol%	—	—	—	3	0·2	0·1

value of the open porosity was a crude indicator of the extent of densification. A qualitative characterization of crystalline phases was performed by X-ray diffraction. Microstructural features were observed by SEM on fracture surfaces. The location of intergranular phases and the identification of the crystallized ones were carried out by TEM. Thermal diffusivity was measured by a laser flash method.

3 Results

3.1 Relative density and open porosity

The values of the density and open porosity are shown in Table 2. A low open porosity (<1%) was considered to be associated with a high densification. Small additions of 0·5% C or 0·5% C3S3A are enough to yield full densification of AlN products. CS and CS2A do not act with the same efficiency, and higher amounts are necessary to yield a low porosity. Typical values are between 0·5 and 1 wt% for CS, and between 2 and 4 wt% for CS2A.

3.2 Nature of crystalline phases

For a given sintering aid, the crystallographic nature of the intergranular phases is not very sensitive to concentration unless reaction with the AlN grains develops to a large extent. However, an extensive reaction is not expected to occur owing to the low sintering temperature. The phases identified by X-ray diffraction are given in Table 3.

Table 3. Intergranular phases in AlN with various additives

Additive	*Intergranular phases*	
C	$CaAl_2O_4$	
CS	$CaAl_4O_7$ and/or $Ca_3Al_{10}O_{18}$	$Ca_2SiAl_2O_7$
C3S3A	$CaAl_4O_7$ and/or $Ca_3Al_{10}O_{18}$	27R AlN polytype
CS2A	$CaAl_4O_7$ and/or $Ca_3Al_{10}O_{18}$	27R AlN polytype

3.3 Microstructural features

3.3.1 SEM observations

The microstructures of AlN samples with 0·5 and 6 wt% additions of sintering aids were observed on fracture surfaces. The nature of the additive does not play a significant role in microstructural features. Fracture always occurs in an intergranular mode. Figure 2 shows the microstructures of C–AlN, CS–AlN and C3S3A–AlN materials.

All materials exhibit a low porosity. The grain morphology is not very uniform, the grain size ranging from 3 to 6 μm (0·5 wt% additives) and from 1 to 3 μm (6 wt% additives). This shows that a higher additive concentration inhibits grain growth.

3.3.2 TEM observations

TEM was used to study materials with 2 and 6 wt% of C or CS additions.

For low additive concentrations (2 wt%), secondary phases are segregated at triple points (Fig. 3(a)) and the grain boundaries themselves seem to be rather free of segregations. $Ca_2SiAl_2O_7$ and $CaAl_4O_7$ are the compositions of secondary phases when CS is the sintering aid, whereas $CaAl_2O_4$ is the only phase when C is the additive. Crystallographic structures are tetragonal, monoclinic and orthorhombic, respectively. No crystalline nitrogen-containing phases were detected. However, the presence of some residues of nitrogen-containing glasses is not excluded.

For higher additive concentrations (6 wt%), secondary phases are segregated both at triple points and along the grain boundaries (Fig. 3(b)). Moreover, the $Ca_2SiAl_2O_7$ phase in 6% CS–AlN materials precipitates in the form of tetragonal paving blocks. Fringe contrasts (Fig. 3(c)) are characteristic of polytypes.

In all cases, planar defects and dislocations are observed in AlN grains (Fig. 3(d)). Their density does not appear to be a function of the nature and amount of additives.

3.4 Thermal properties

The thermal conductivity (W m^{-1} K^{-1}) of sintered samples is expressed by the following equation:

$$\lambda = 100 a \rho C_p$$

where a is thermal diffusivity (cm^2 s^{-1}), ρ is density (g cm^{-3}) and C_p is heat capacity (J g^{-1} K^{-1}).

The assumption is that the heat capacity variation in relation to the additive content is low in the concentration range that is used, which is in agreement with Braudeau's data[15] on Y_2O_3–AlN.

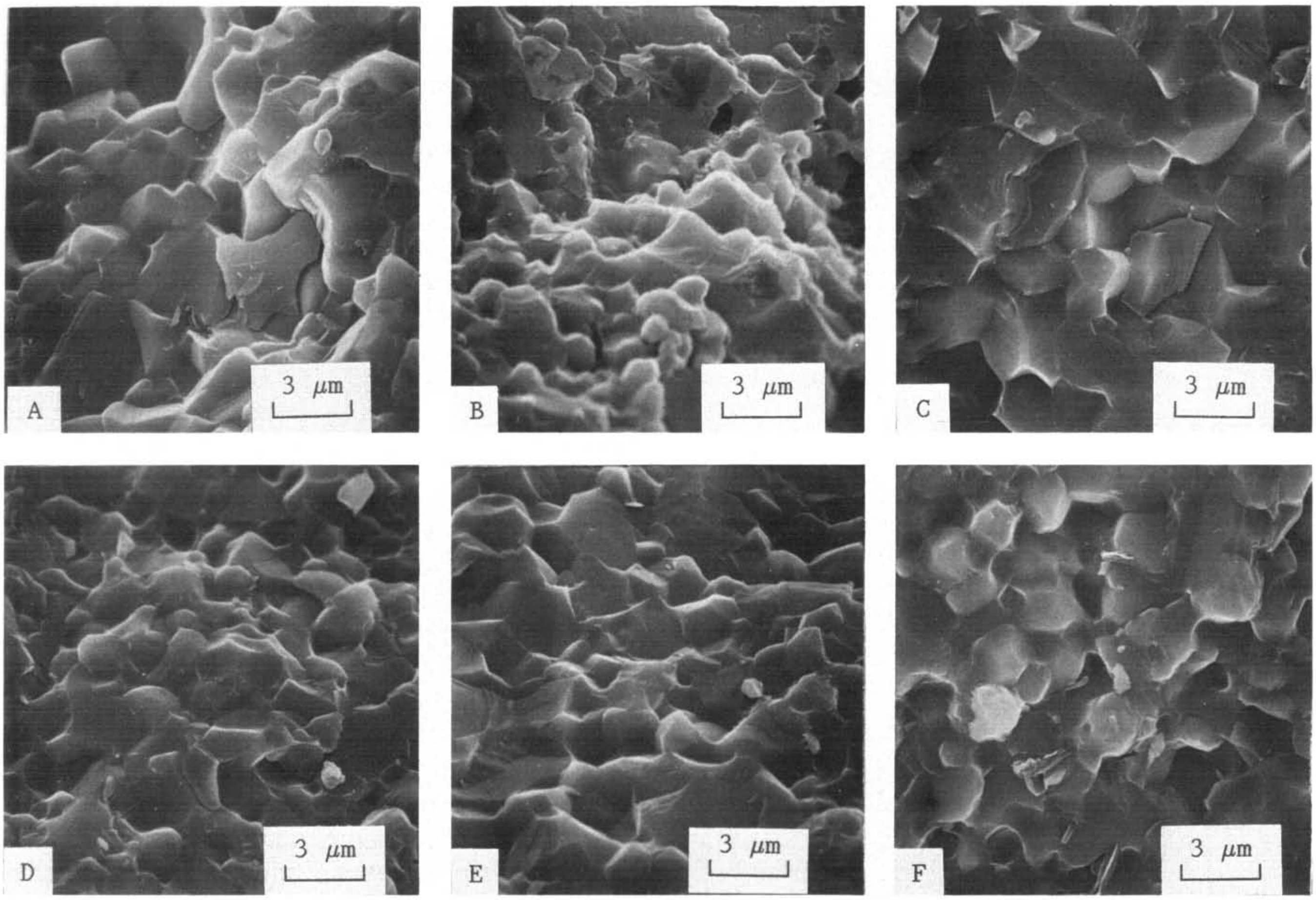

Fig. 2. SEM observations: A, B, C, D, E and F refer to 0·5 wt% C–AlN, 6 wt% C–AlN, 0·5 wt% CS–AlN, 6 wt% CS–AlN, 0·5 wt% C3S3A–AlN and 6 wt% C3S3A–AlN materials, respectively.

Thermal conductivity is therefore always determined by taking the heat capacity value of pure, dense aluminium nitride (0·734 J g^{-1} K^{-1} at 20°C).

Table 4 shows that thermal conductivity depends on the nature and the concentration of sintering aids. For all additives, thermal conductivity begins to increase as the additive content increases, reaches a maximum and then decreases gradually. For Cα, the maximum thermal conductivity is not observed at the same additive content as the maximum apparent density. For the three other additives, on the contrary, the maximum conductivity virtually corresponds to the maximum apparent density.

Table 4. Influence of additives on thermal properties of AlN

Materials		*Additive content (wt%)*					
		0·5	*1*	*1·5*	*2*	*4*	*6*
C–AlN	λ(W m^{-1} K^{-1})	58	61	70	61	54	25
	P_0 vol%	0·1	0·25	0·7	0·5	0·6	3
CS–AlN	λ(W m^{-1} K^{-1})	36	40	45	50	49	41·5
	P_0 vol%	1·5	0·5	0·3	0·3	0·1	0·3
C3S3A–AlN	λ(W m^{-1} K^{-1})	60	54	52	52	42	35·5
	P_0 vol%	0	0	0·1	0·1	0·4	2·5
CS2A–AlN	λ(W m^{-1} K^{-1})	—	—	—	44	45	38·5
	P_0 vol%	—	—	—	3	0·2	0·1

4 Discussion

4.1 Densification

The use of $CaCO_3$ as a sintering aid leads to liquid formation at temperatures as low as 1400°C in the CaO–Al_2O_3 system. The liquid solidifies into the $CaAl_2O_4$ aluminate during cooling. It has also been indicated that some AlN dissolution could occur.[14] A low amount of $CaCO_3$ ($<$0·5%) is enough to yield very dense AlN materials with open porosity below 0·1%.

The use of CS, C3S3A or CS2A as sintering aids leads to the formation of liquids at temperatures of 1400, 1587, 1600 and 1553°C in the systems CaO–Al_2O_3, CaO–SiO_2, SiO_2–Al_2O_3 and CaO–SiO_2–Al_2O_3, respectively. This shows that wollastonite (CS) is the most efficient additive for decreasing the liquid formation temperature.

As far as the nature of secondary phases is concerned, CS leads to $CaAl_4O_7$ and $Ca_2SiAl_2O_7$

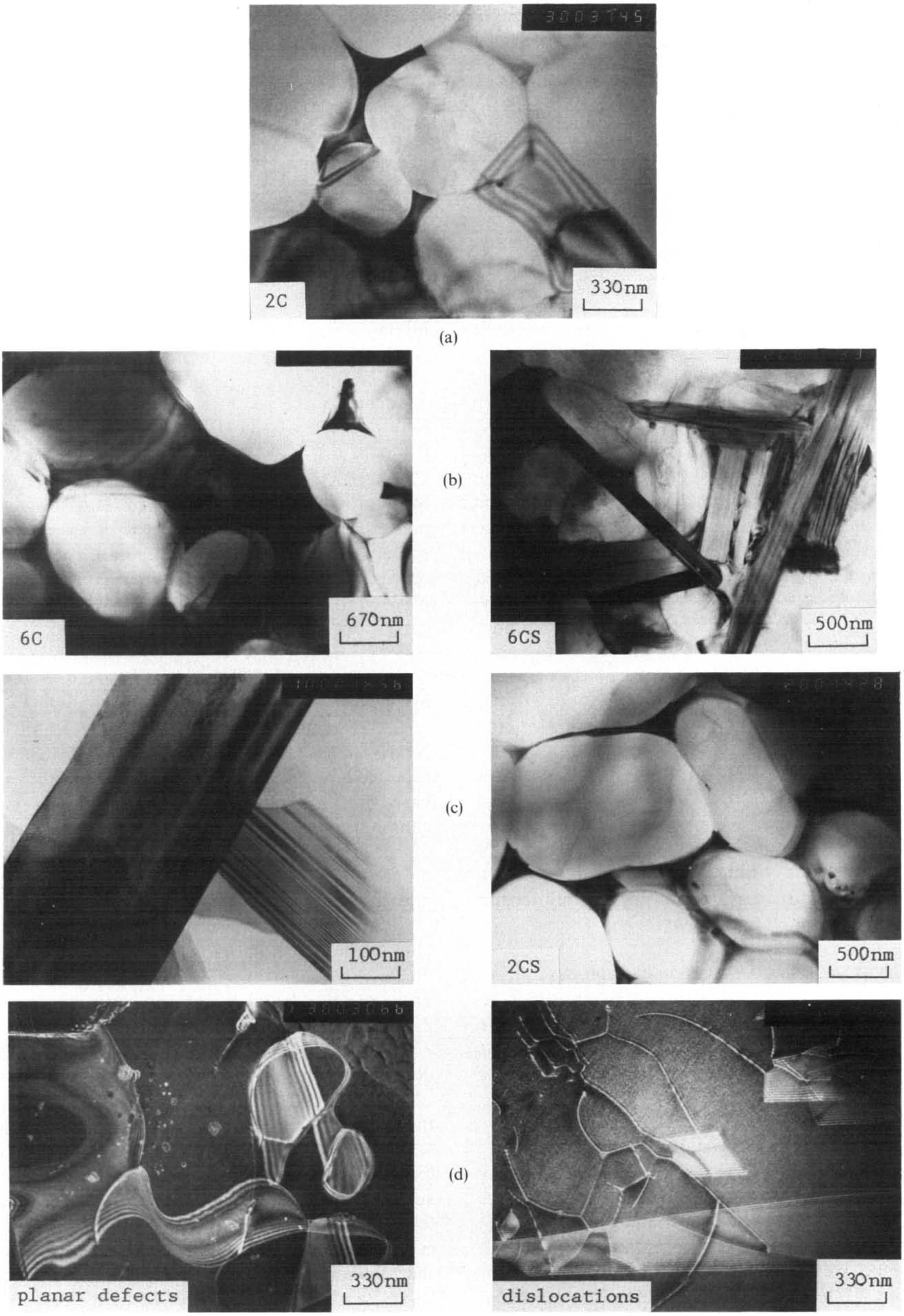

Fig. 3. (a) TEM observations: 2C and 2CS refer to 2 wt% C–AlN and 2 wt% CS–AlN materials, respectively. (b) TEM observations: 6C and 6CS refer to 6 wt% C–AlN and 6 wt% CS–AlN materials, respectively. (c) TEM observation: fringe contrast in the $Ca_2SiAl_2O_7$ blocs, which appears in 6 wt% CS–AlN material. (d) TEM observation: planar defects and dislocations observed in AlN grains.

phases, while C3S3A and CS2A lead to $Ca_3Al_{10}O_{18}$ and/or $CaAl_4O_7$ phases and the 27R AlN polytype. This shows that, in contrast to what is observed for CS, SiO_2 does not react with the alumina present at the surface of nitride grains to form phases in the $CaO–SiO_2–Al_2O_3$ system but directly reacts with AlN to form the 27R polytype.

4.2 Thermal conductivity of AlN materials

The highest thermal conductivity values here are 70 and 50 $W m^{-1} K^{-1}$ for C–AlN and CS–AlN materials, respectively. For C–AlN, the maximum thermal conductivity is obtained for a higher additive content than the maximum density. This shows that intergranular phases are not necessarily detrimental to the thermal conductivity of sintered materials. By analogy with the role of Y_2O_3 additives,[6] it is thought that the eutectic liquid cleans the surface of AlN grains and therefore prevents oxygen from entering the AlN lattice. For excessive additive contents, however, the conductivity decrease must be due to the thermal barriers associated with the secondary phase segregation. For low additive contents, secondary phases are precipitated at triple points only, and they do not scatter phonons severely. For high additive contents, on the contrary, secondary phases form a continuous layer around AlN grains, and they scatter phonons at the interfaces. In the case of C3S3A–AlN and CS2A–AlN materials, the 27R AlN polytype could be a supplementary cause for the degradation of thermal conductivity.[16]

The possible influence of planar defects in AlN grains was not studied. As previously stated, however, the defect density does not sensibly depend on the sintering aids.

4.3 Thermal properties of secondary phases

Secondary phases were synthesized in order to determine their intrinsic thermal conductivity. The apparent and theoretical density, open porosity, heat capacity and thermal conductivity are given in Table 5. The heat capacity values for sintered aluminates were evaluated by a rule of mixtures.

The $CaAl_4O_7$, $Ca_3Al_{10}O_{18}$ and $Y_3Al_5O_{12}$ compounds were poorly densified after a sintering at 1680°C. The open porosities are in the order of 10 vol%. On the contrary, the $CaAl_2O_4$, $Ca_2SiAl_2O_7$ and Al_2O_3 compounds were well densified, with open porosities between 0·3 and 3·4 vol% only. If the density fluctuations are not taken into account in a specific manner, it can be seen that all aluminates exhibit a lower thermal conductivity than alumina. However, the $Y_3Al_5O_{12}$ phase exhibits rather a high value of 9 $W m^{-1} K^{-1}$, which confirms that yttria is more favourable than the other additives from this point of view. The thermal conductivity of $CaAl_2O_4$ (formed in C–AlN) is lower than that of $CaAl_4O_7$ and $Ca_3Al_{10}O_{18}$ (formed in CS–AlN, C3S3A–AlN and ACS2–AlN). The use of CS, C3S3A and CS2A additives leads to the formation of $Ca_2SiAl_2O_7$ and/or 27R AlN polytype phases. The presence of a phase with a low volume content is not expected to reduce the thermal conductivity in a dramatic manner. However, it can play a role in the fall of conductivity of the corresponding AlN materials.

Table 5. Characteristics of secondary phases

Material	ρ ($g cm^{-3}$)	P_0 (%)	d_{th}	C_p ($J g^{-1} K^{-1}$)	λ ($W m^{-1} K^{-1}$)
Al_2O_3	3·91	0·3	3·965	0·78	23
$CaAl_2O_4$	2·84	3·4	3·22	0·75	3
$CaAl_4O_7$	2·44	12·5	3·44	0·76	5
$Ca_3Al_{10}O_{18}$	2·58	8·9	3·38	0·74	5
$Ca_2SiAl_2O_7$	2·81	2	2·96	0·74	1·5
$Y_3Al_5O_{12}$[a]	3·89	11·4	4·50	0·59	9

[a] The $Y_3Al_5O_{12}$ compound appears in $AlN + Y_2O_3$ materials when less than 10 wt% of additive is used.[17]

5 Conclusion

Nearly dense aluminium nitride substrates were produced by tape casting and sintering of AlN-based materials. $CaCO_3$ and $3CaO–3SiO_2–Al_2O_3$ compounds are efficient sintering aids. An amount of 0·5 wt% of these additives allows the sintering to proceed at 1650°C and leads to a negligible open porosity.

$CaSiO_3$ leads to a reaction between silica and the alumina present at the surface of AlN grains. $3CaO–3SiO_2–Al_2O_3$ and $CaO–2SiO_2–Al_2O_3$ lead to a direct reaction between silica and AlN, to form the 27R AlN polytype.

The thermal conductivity of sintered materials depends on the thermal conductivities and distribution of intergranular phases. The highest value of thermal conductivity (70 $W m^{-1} K^{-1}$) is obtained with 1·5 wt% $CaCO_3$ as a sintering aid. The additive forms a liquid phase, which is thought to clean the surface of nitride grains and hence to prevent oxygen from entering the AlN lattice. However, the additive concentration must be rather low, in order that all the secondary phase ($CaAl_2O_4$) is located at the triple points. Higher additive contents lead to the wetting of grains by the secondary phase, which results in a conductivity decrease. Other additives are less favourable than $CaCO_3$, owing to the formation of low conductivity $Ca_2SiAl_2O_7$ and 27R AlN polytype phases.

The present work has shown the influence of simple additives. However, a recent paper[18] has indicated that AlN can be sintered at 1600°C with a complex additive of Y_2O_3, CaO, La_2O_3, CeO_2 and SiO_2. This paper has also confirmed that low levels of SiO_2 are beneficial to the liquid-assisted densification. All these data confirm that AlN substrates could be produced in economical conditions.

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