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Effects of Reduction of the Al–Y–O Containing Secondary Phases During Sintering of AlN with YF_3 Additions

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Abstract

The effect of reduction of the Al–Y–O containing secondary phases forming AlN and YN during sintering of AlN(YF_3) embedded in AlN powder has systematically been studied. The sintering was performed in a graphite furnace at 1880°C. With increased reduction of the secondary phase, the following effects were observed: (a) the chemical composition of the secondary phase changed in the order $YAG \rightarrow YAP \rightarrow YAM \rightarrow Y_2O_3 \rightarrow YN$; *(b) reduction of the amount or removal of the secondary phase; (c) decreased sinterability of AlN when more than 5 wt% YF_3 was added; (d) reduction in the lattice oxygen content; and (e) increased thermal conductivity. Included in the paper is a discussion of a possible mechanism for the reduction of the secondary phase, which we propose is controlled by the diffusion of gas species (CO/CO_2 and/or Al_2O) through the powder bed and the distance between the AlN samples and a graphite source, as well as a proposed optimal sintering programme for AlN with Al–Y–O containing phases.*

1 Introduction

Aluminium nitride (AlN) has attracted much attention, mainly because of its high thermal conductivity. Slack *et al.*[1] estimated the thermal conductivity of an AlN single crystal to be 319 W m^{-1} K^{-1}; however, polycrystalline materials have much lower thermal conductivity (120–240 W m^{-1} K^{-1}) because of oxygen impurities and microstructural defects.

Y_2O_3 and YF_3 are among the most common sintering additives used during liquid-phase sintering of AlN ceramics because a liquid dissolving AlN is formed at the eutectic temperature in the system Al_2O_3–Y_2O_3. Al_2O_3 is normally present as a surface layer of the AlN grains. During heating an Al–Y–O containing phase is formed at around 1100°C due to reaction between the oxide surface layer of the AlN grains and the Y_2O_3/YF_3 additive.[2] The eutectic temperature is around 1800°C,[3] and hence liquid-phase sintering of AlN with Y_2O_3 or YF_3 additives has to be done at a temperature above some 1800°C. The sintering of AlN is most often performed in a nitrogen atmosphere in a graphite furnace using different kinds of crucibles (C, AlN or BN) with or without a protective powder bed (AlN) around the samples.[2,4–13] AlN with Y_2O_3 or YF_3 additives, sintered at the described conditions, contains a range of different secondary phases: $Al_5Y_3O_{12}$ (YAG), $AlYO_3$ (YAP), $Al_2Y_4O_9$ (YAM), Y_2O_3 and YN.[2,4–13] The reducing atmosphere most often present in a graphite furnace due to oxygen impurities, thermal decomposition and/or reduction of oxides is reported to reduce the Al–Y–O containing secondary phases.[5–8,10,12,13]

In this work we have done a systematic study of how the reduction of the Al–Y–O containing secondary phases influences the density, amount and distribution of secondary phases, thermal conductivity and oxygen content of the sintered AlN samples. YF_3 was used as sintering additive to avoid additional oxygen content in the AlN ceramics and to be able to visualize the effect of the reduction of the secondary phase more clearly.

2 Experimental

AlN powder (Tokuyama Soda, grade F) with 0·9 wt% (0·3 wt% lattice dissolved) oxygen and a specific surface area of 3·4 m^2 g^{-1} was used. YF_3 (Pennwalt, 99·99% purity) was used as sintering

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additive. Five different compositions of samples were used, i.e. with 1, 2, 3, 5 and 10 wt% YF_3. Green bodies of AlN were prepared by a slip-casting technique using isopropanol and the dispersing agent Alkasurf SS-0-75 (Alkaril Chemicals). Mixing of the slurry was performed by an ultrasonic disintegrator (MSE Soniprep 150). All stages in the processing of the green bodies were performed in a dry nitrogen atmosphere glove box (H_2O < 20 ppm) to control the oxygen and impurity content. The green bodies were about 1·5 cm in diameter and 1 cm in height. Before sintering the dispersing agent was removed during 20 h of heating at 150°C in flowing nitrogen. The green density of the samples was about 1·5 g cm^{-3}. The samples were sintered in a nitrogen atmosphere (<5 ppm O_2) in a graphite furnace (total volume about 80 l) at 1880°C for 2 or 6 h. For convenience, the sintering was done with nitrogen flowing through the furnace; however, the gas inlet and outlet were far from the crucible so we can assume stationary conditions around the samples during the sintering.

Three different sintering conditions were employed as shown in Fig. 1: in condition A the AlN sample is embedded in a 'fine' AlN powder bed (grain size <15 μm) in a BN crucible covered by a BN lid (not gastight); in condition B the AlN sample is embedded in a 'coarse' AlN powder bed (grain size <0.5 mm) in a BN crucible covered by a BN lid (not gastight); and in condition C the AlN sample is embedded in a 'fine' AlN powder bed (grain size <15 μm) in a graphite crucible without a lid. The 'fine' powder bed used for sintering condition A reached a higher degree of densification than the 'fine' powder bed used for sintering condition C during the firing. The crucible outer diameter was 52 mm and the height was 64 mm.

The densities of the sintered samples were measured by the liquid immersion method (ASTM C737) using isopropanol. The microstructure was investigated by scanning electron microscopy (SEM) (Zeiss DSM 940). Secondary phases were analysed by a Teller diffractometer (Philips PW 1730/10) and EDS (Noran Instruments, Tracor Series 2). The thermal conductivity was measured to an accuracy within 10% by a laser flash method using a CO_2 laser (Tac 2, 215G). The oxygen content (total and lattice dissolved) was determined by selective hot gas extraction method using a LECO TC 436 analyser by a procedure similar to that described by Thomas and Müller.[14,15] The method allows for separate determination of the lattice dissolved oxygen, oxygen in the secondary phase and the oxygen adsorbed on the surface of the AlN ceramics. The total oxygen content was determined by mixing the AlN samples (crushed <20 μm) with a graphite powder (LECO 501-073) in a nickel basket (LECO 763-065). The nickel basket was placed within a graphite crucible (LECO 782-720) and heated at 2700°C for 50 s. The oxygen content adsorbed on the surface and the oxygen dissolved in the secondary phase were determined by slow heating (6 K s^{-1}) of the AlN samples (ground <20 μm) mixed with graphite powder only in the graphite crucible. The amount of oxygen in the AlN lattice was calculated by difference.[14,15] Typical experimental curves for determination of the total oxygen content and the oxygen content adsorbed on the surface and dissolved in the Al–Y–O secondary phases are given in Fig. 2.

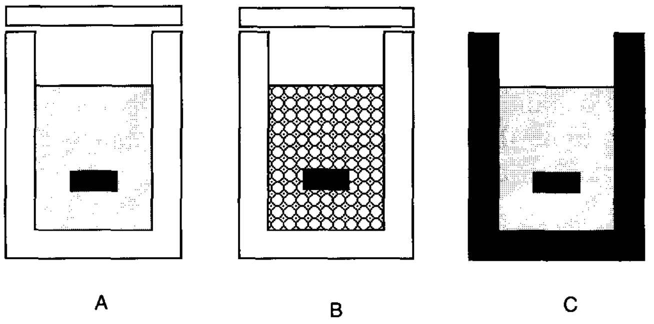

Fig. 1. Schematic representation of the three different sintering conditions. A: AlN sample embedded in a 'fine' AlN powder bed in a BN crucible with a BN lid; B: AlN sample embedded in a 'coarse' AlN powder bed in a BN crucible with a BN lid; C: AlN sample embedded in a 'fine' AlN powder bed in a carbon crucible without a lid.

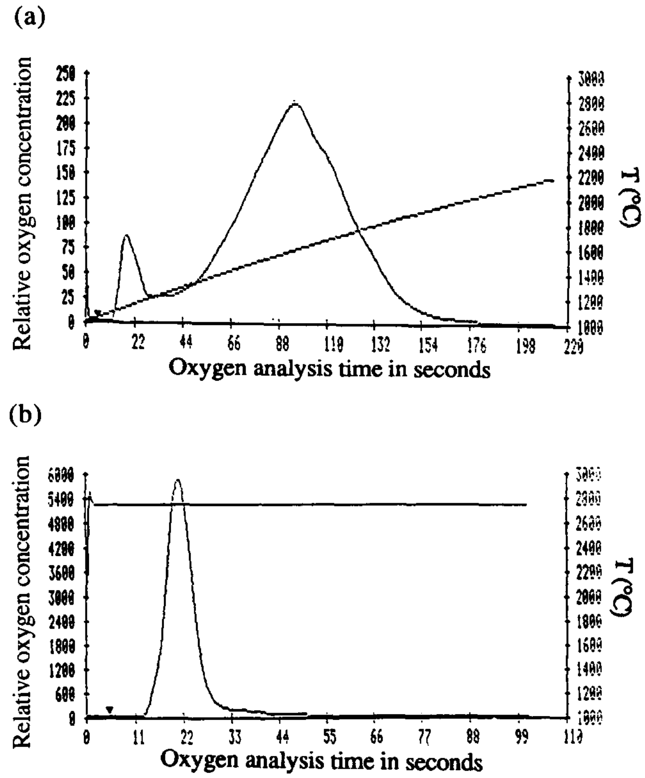

Fig. 2. Experimental curves for determination of the oxygen contents in the AlN ceramics by LECO. (a) Release of oxygen adsorbed on the surface and dissolved in the Al–Y–O secondary phase by slow heating (6 K s^{-1}) and (b) constant heating of the AlN sample at 2700°C for determination of the total oxygen content of the AlN sample.

3 Results and Discussion

3.1 Reduction of the Al–Y–O containing secondary phases

As mentioned above, YF_3 in amounts from 1 to 10 wt% was added to the samples as sintering aid. During heating of the green bodies, Y_2O_3 was presumably formed according to:

$$2YF_3(l) + Al_2O_3(s) = 2AlF_3(g) + Y_2O_3(s) \quad (1)$$

The melting point of YF_3 is reported to be 1155°C.[16] Some YF_3 might evaporate; however, most YF_3 is supposed to react with Al_2O_3 and form $AlF_3(g)$ (AlF_3 sublimes at 1246°C at normal pressure) because only trace amounts of YF_3 were detected in the deposit in the colder regions of the furnace. The evaporation of AlF_3 probably takes place before the AlN powder bed and the AlN samples are densified, because the first maximum in the densification rate of AlN(Y_2O_3) has been observed in the range from 1400°C.[10] However, most of the densification takes place between 1750 and 1800°C,[10] which is well above the sublimation temperature for AlF_3. AlF_3 was deposited as a white powder in the colder regions of the furnace. Other phases observed in trace amounts in the colder regions of the furnace were Y_2O_3 (hexagonal) and AlN. The weight loss of the AlN samples due to thermal decomposition of AlN(s) is considered to be negligible since the protecting embedding was used.

The secondary phases present in the bulk and on the surface of the AlN samples after sintering at conditions A, B and C are shown in Table 1. The secondary phases present in the samples sintered at condition A were generally more rich in Al_2O_3 than the secondary phases in the corresponding samples sintered at condition B. For the samples sintered at condition C a significant difference between the secondary phases on the surface and in the bulk was observed. After 2 h of sintering only Y_2O_3 and YN were identified on the surface, while some Y–Al–O containing phases were present in the bulk. However, after 6 h of sintering, only YN was found on the surface and the bulk was almost completely free of secondary phases with addition of 1 to 3 wt% YF_3. The changes observed in the composition of the secondary phases result from reduction of the Al–Y–O containing phases forming AlN and YN. YN was never observed together with Al_2O_3, in accordance with the phase diagram presented by Sun *et al.*,[17] which stated that YN and Al_2O_3 are not coexistent.

In the following, a discussion of the mechanism for the reduction of the Al–Y–O containing phases is given based on chemical equilibria. For the thermodynamic calculations data are taken from Barin.[16] The sintering temperature (1880°C) is above the eutecticum of the Al_2O_3–Y_2O_3 system;[3] however, the Al–Y–O phases will here be considered as solid species (Al_2O_3 and Y_2O_3) because thermodynamic data are not present in the literature for the liquid phase.

The surface layer of Al_2O_3 on the AlN grains might react with AlN according to:

$$Al_2O_3(s) + 4\,AlN(s) = 3Al_2O(g) + 2N_2(g) \quad (2)$$

The equilibrium pressure of $Al_2O(g)$ at 1880°C and 1 atm N_2 is calculated to be 2×10^{-4} atm. However, due to the small AlN grain size used and the fact that the liquid phase formed is wetting the AlN grains, the partial pressure of $Al_2O(g)$ above the liquid is supposed to be smaller than calculated from the equilibrium due to capillary forces. For reaction (2) to proceed, the $Al_2O(g)$ formed has to be removed from the AlN samples diffusing through the protective AlN powder bed and react with carbon present in the furnace or on the outer graphite crucible (see Fig. 1) to reform AlN according to:

$$Al_2O(g) + C(s) + N_2(g) = 2AlN(s) + CO(g) \quad (3)$$

Using the equilibrium pressure of $Al_2O(g)$ from eqn (2), the calculated equilibrium pressure of CO for eqn (3) is 3.3 atm, and hence the equilibrium position of reaction (3) is driven towards the formation of AlN. However, due to the use of embedding of the samples, the partial pressure of $Al_2O(g)$ at the surface of graphite is much lower

Table 1. Secondary phases present in AlN samples sintered at condition A, B and C. Phases in brackets are observed in trace amounts

Additive YF_3 (wt%)	*Condition A*		*Condition B*		*Condition C*			
	2 h	*6 h*	*2 h*	*6 h*	*2 h surface*	*2 h bulk*	*6 h surface*	*6 h bulk*
1	(YAG)	(YAG)	YAP,YAM	YAM(YAP)	Y_2O_3,YN	YAG	YN	(YN)
2	YAG	YAG	YAM	YAM	Y_2O_3,YN	YAM(YAG)	YN	(Y_2O_3,YN)
3	YAG	YAG	YAP(YAM)	YAP	Y_2O_3,YN	YAP,YAM	YN	(YN)
5	YAG	YAG	YAP(YAM)	YAM(YAP)	Y_2O_3YN	Y_2O_3	YN	Y_2O_3,YN
10	Y_2O_3,YAM	Y_2O_3	YN,Y_2O_3	Y_2O_3	Y_2O_3,YN	Y_2O_3,YN	Y_2O_3,YN	Y_2O_3,YN

than assumed above. The total reaction [eqns (2) and (3)] is:

$$Al_2O_3(s) + 3C(s) + N_2(g) = 2AlN(s) + 3CO(g) \quad (4)$$

It is believed that the rate-determining step for this proposed reaction mechanism (mechanism 1) is the diffusion of the $Al_2O(g)$ through the AlN powder bed towards the graphite source. As the sintering condition is changed from A to B, the diffusion of $Al_2O(g)$ from the AlN samples towards the graphite outside the BN crucible becomes more easy due to less packing density of the AlN powder bed at sintering condition B compared with A. Hence, the secondary phases present in the AlN samples sintered at condition A were more rich in Al_2O_3.

As reaction (4) proceeds, CO gas is formed. From the maximum oxygen content in the nitrogen gas used, the estimated partial pressure of CO in the furnace at the start of the sintering was less than 10^{-5} atm. If all the Al_2O_3 present in the samples and in the powder bed reacted according to reaction (4), the partial pressure of CO in the furnace would be about 10^{-2} atm assuming no flow of nitrogen through the furnace and no pressure gradients in the crucible/furnace. Therefore, quite a high partial pressure of CO might be developed locally inside the crucible especially at sintering condition C, where large amounts of secondary phases were reduced.

Another proposed mechanism is that the CO gas formed might diffuse through the powder bed and react with the $Al_2O(g)$, $Al_2O(g)$ adsorbed on Al_2O_3 or Al_2O_3 in the liquid phase according to eqn (5). For simplicity the reacting aluminium-containing species is assumed to be $Al_2O_3(s)$:

$$Al_2O_3(s) + 3CO(g) + N_2(g) = = 2AlN(s) + 3CO_2(g) \quad (5)$$

The calculated equilibrium pressure of CO_2 is 5×10^{-10} atm at 10^{-5} atm CO, which was assumed to be the partial pressure of CO in the furnace due to oxygen impurities. This partial pressure of CO_2 is so low that eqn (5) will not make a significant contribution to the reduction of Al_2O_3. However, CO gas is produced from eqn (3) and this will locally (in the crucible) give a much higher partial pressure of CO and eqn (5) might be of importance. The CO_2 gas formed will diffuse out of the powder bed and react with carbon (crucible/furnace interior) according to:

$$CO_2(g) + C(s) = 2CO(g) \quad (6)$$

For each mole of CO_2 formed, two moles of CO are gained. This means that the partial pressure of CO will increase exponentially if the reaction first is initiated. For this possible reaction mechanism (mechanism 2), the rate-limiting step is believed to be the diffusion of the gas species CO/CO_2 through the AlN powder bed or the limitation might be the equilibrium of eqn (5). Equations (5) and (6) give the same total reaction given in eqn (4). A crucial difference between the reduction of Al_2O_3 according to mechanism 1 [eqns (2) and (3)] and mechanism 2 [eqns (5) and (6)] is where the AlN is formed. According to mechanism 1, AlN is formed on the solid carbon (colder regions of the furnace/crucible). For mechanism 2, the AlN is formed inside or on the surface of the AlN samples. Only very small amounts of AlN were found (identified by X-ray diffraction) deposited on one of the upper radiation shields in the graphite furnace. No broad peaks due to amorphous material were observed in the X-ray diffractograms. These small amounts of AlN could not account for the total amount of Al_2O_3 reduced, especially at sintering condition C. Hence, reduction of Al_2O_3 according to mechanism 2 [eqns (5) and (6)] was probably more important than the reduction according to mechanism 1 [eqns (2) and (3)], especially at sintering condition C. The assumption, stating the importance of the CO gas as the reducing species is strengthened by the detection of CO and CO_2 by mass spectrometry in $AlN(Y_2O_3)$ ceramics reported by Watari *et al.*[6]

In recent work Mitra *et al.*[18] heat-treated dense AlN ceramics with Al–Y–O containing secondary phases at 1900°C for 2 h in a pure nitrogen atmosphere in a W furnace and hence no reducing atmosphere was present. They did not use any embedding of the samples during the heat treatment. Even if their interpretation of the data is questionable, they did not observe a complete depletion of the Al_2O_3 in the secondary phase during this heat treatment or a reduction in the amount of lattice dissolved oxygen which was observed for sintering condition C in this work. We propose that this observed difference is due to the presence of the reducing atmosphere in our work and the significance of CO as a reducing species.

At sintering condition C even large amounts of Y_2O_3 were reduced to YN when all Al_2O_3 was removed from the sample. The total reaction for the reduction of Y_2O_3 is given in eqn (7), where we propose a similar scheme for the reduction of Y_2O_3 with CO as the reducing species to reaction mechanism 2 discussed for Al_2O_3. It should be kept in mind that the partial pressure of CO is considerably higher at the beginning of the reduction of Y_2O_3 compared with Al_2O_3. Large amounts of YN were observed on the surface of the AlN samples, and hence the reducing agent (proposed as CO) must have been present at the surface of the AlN sample during the reduction of the Y_2O_3.

$$Y_2O_3(s) + 3C(s) + N_2(g) = 2YN(s) + 3CO(g) \quad (7)$$

The possibility for forming volatile Y–O species over Y_2O_3, like $Al_2O(g)$ in the Al_2O_3 system, was also examined. The partial pressure of YO(g), which has been found to be the dominant species above $Y_2O_3(s)$ at high temperature, was calculated to be 10^{-6}–10^{-7} atm at 1880°C using data from Marushkin *et al.*[19] This partial pressure is supposed to be too low to play a major role in the removal of Y_2O_3 from the AlN samples.

To conclude the discussion about the mechanism for the reduction of the Al_2O_3 and Y_2O_3 containing secondary phases in AlN specimens sintered in an AlN powder bed, this reduction is not determined by chemical equilibrium but it is controlled by the diffusion of gas species (i.e. Al_2O and/or CO/CO_2) through the powder bed and the distance between the AlN samples and the graphite source. Therefore, the Al–Y–O containing phases present in the AlN samples sintered at condition A were less reduced than the Al–Y–O containing phases present in the corresponding samples sintered at condition B, due to higher density of the AlN powder bed at sintering condition A. The highly increased reduction of the Al–Y–O containing phases at sintering condition C was probably mainly due to the decreased distance between the AlN samples and the graphite source (the graphite crucible) compared with sintering conditions A and B. We propose reaction mechanism 2 to be dominating at a certain value of the partial pressure of CO (condition C), probably due to a low diffusion rate of $Al_2O(g)$ in the powder bed.

3.2 Densification of the AlN samples

To sinter $AlN(YF_3)$ to nearly 100% density, there has to be Al_2O_3 present as a surface layer on the AlN grains to form a liquid phase in the Al_2O_3–Y_2O_3 system at the sintering temperature. A change in the amount of Al_2O_3 will influence the amount of liquid phase at 1880°C.[3] Using YF_3 as the sintering additive the liquid phase becomes more Y-rich (Y_2O_3 or YN) through two chemical reactions: (a) by reaction between $YF_3(l)$ and $Al_2O_3(s)$ to form $AlF_3(g)$ and $Y_2O_3(s)$ [eqn (1)] and (b) by reduction of Al_2O_3.

Addition of less than 5 wt% YF_3 gave AlN ceramics with densities above 97% for all sintering conditions (Fig. 3). When 5 wt% YF_3 was added, all the Al_2O_3 (about 0·6 wt%) from the surface of the AlN grains should theoretically be removed according to eqn (1), assuming no evaporation of YF_3. This complete removal is not likely to occur because the YF_3 in the green body is not in contact with all the AlN grains. Anyway, the

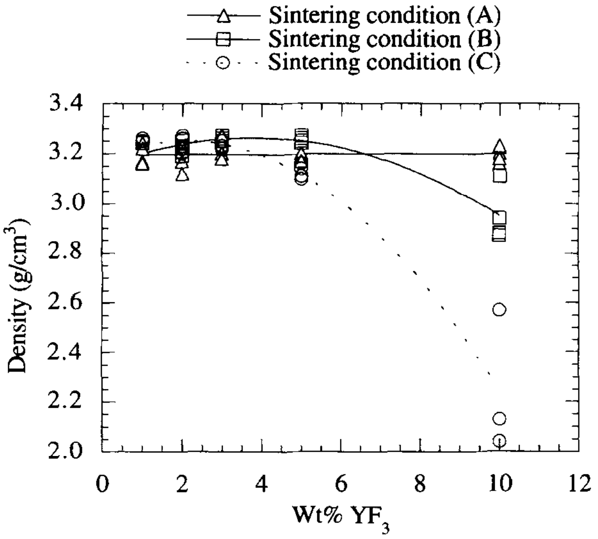

Fig. 3. Density of AlN samples sintered for 6 h as a function of sintering conditions and amount of YF_3 added. The lines are drawn as a guide to the eye.

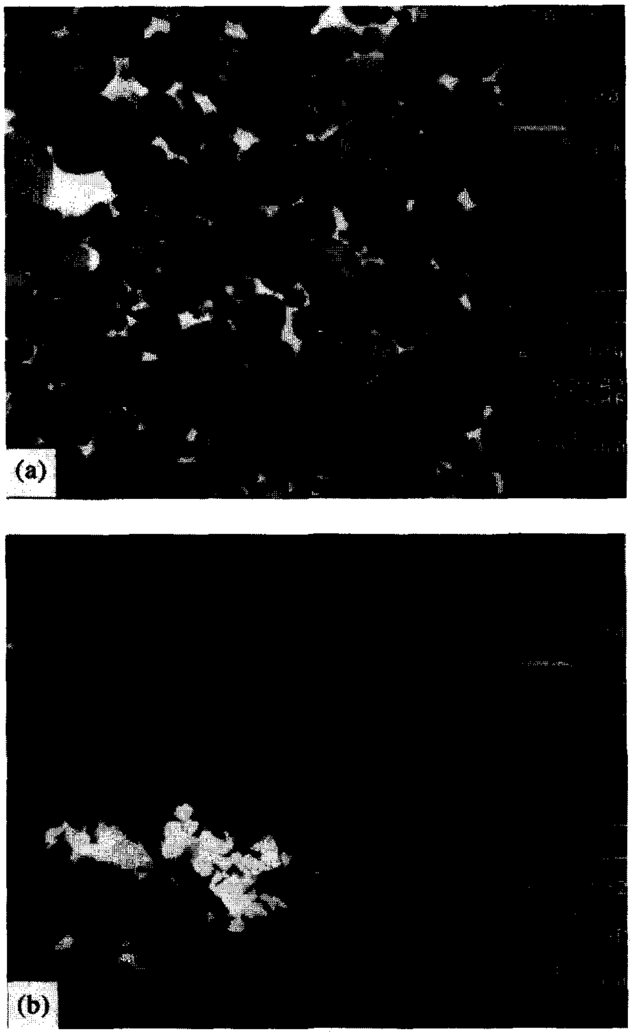

Fig. 4. SEM fractographs of AlN (10 wt% YF_3) samples with electron-backscatter contrast between Y-containing phases (bright) and the AlN grains (dark): (a) sintering condition A; (b) sintering condition C.

amount of Al_2O_3 on the AlN surface will be greatly reduced when the amount of YF_3 added is increasing and a more Y_2O_3-rich secondary phase will be formed. In this situation the influence of the sintering conditions gave rise to large differences in the density and the microstructure, see Figs 3 and 4, respectively. Figure 4 shows fracture surfaces of AlN samples with 10 wt% YF_3 added and sintered at condition A and C for 2 h. The sample sintered at condition A [Fig. 4(a)] shows a well distributed secondary phase (YAM and Y_2O_3) which indicates formation of a liquid phase during the sintering. The sample sintered at condition C [Fig. 4(b)] shows open porosity and an inhomogeneous distribution of the secondary phase (YN and Y_2O_3), which indicate that no/little liquid phase was formed during the sintering. The absence of a liquid phase at the sintering temperature reduces the additional driving force for densification of AlN, which is attained by the liquid-phase mechanism. This explains the reduced density observed for samples with large additions of YF_3 and sintered at condition C (and condition B), (Fig. 3).

3.3 Oxygen content and thermal conductivity of the AlN samples

Previously, increased amount of additive, increased sintering time and type of furnace (C, W, Mo and HIP) were shown to influence the oxygen content in AlN ceramics.[9,11-13,20] The total oxygen content of the AlN samples is given in Table 2 for the samples sintered for 6 h at condition A, B and C, while the oxygen content dissolved in the AlN lattice is given in Fig. 5. The oxygen content in the AlN lattice is found to decrease as a function of increased reduction of the secondary phases, increased amount of additive and increased sintering time. An experimental correlation is found between the composition of the secondary phases present in the AlN ceramics and the oxygen content in the AlN lattice. Samples sintered at condition A contained YAG only as the secondary phase. The oxygen (lattice) content in these samples seems to approach a value of around 0·2 wt% oxygen. The samples sintered at condition B contained YAP and YAM. The oxygen content in the AlN lattice reaches a lower value, around 0.1 wt% oxygen. In the samples sintered at condition C, YN and Y_2O_3 were present and the oxygen content approaches zero. The oxygen content of the sample with 5 wt% YF_3 and sintered at condition C is not included in Fig. 5 due to the decreased density of this sample. The presence of the more Al_2O_3-rich secondary phases together with the higher level of oxygen in the AlN grains are in accordance with a thermodynamic model proposed by Virkar *et al.*[4] In this model the lower level of Al_2O_3 in the AlN lattice was determined by the activity of Al_2O_3, $a_{Al_2O_3}$, in the secondary phases. The equilibrium activity of Al_2O_3 dissolved in AlN should be highest in samples containing secondary phases in the region Al_2O_3–YAG and lowest in the region YAM–Y_2O_3.

Table 2. Oxygen content ($[O]_{total}$ in wt%) in AlN samples sintered for 6 h at different sintering conditions

Additive YF_3 (wt%)	*Condition A*	*Condition B*	*Condition C*
1	0·94	0·70	0·28
2	1·10	0·50	0·25
3	0·97	0·61	0·14
5	1·29	0·92	0·25
10	0·90	0·92	–

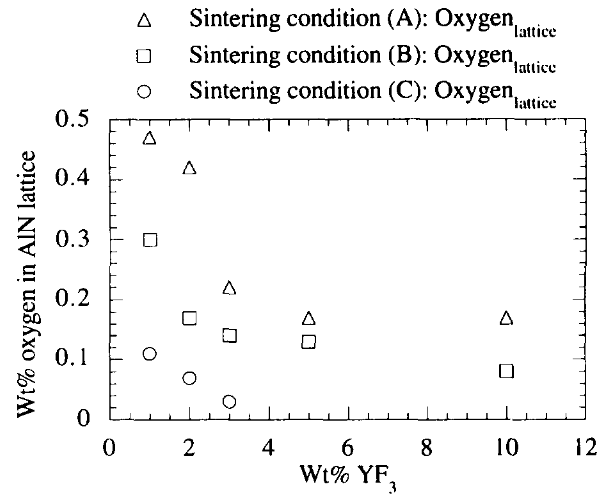

Fig. 5. Oxygen content in the AlN lattice in AlN samples with added YF_3 and sintered for 6 h at condition A, B and C.

The thermal conductivities of the AlN samples sintered for 6 h at different sintering conditions are given in Fig. 6. Two trends are predominant: (a) the thermal conductivity increases going from

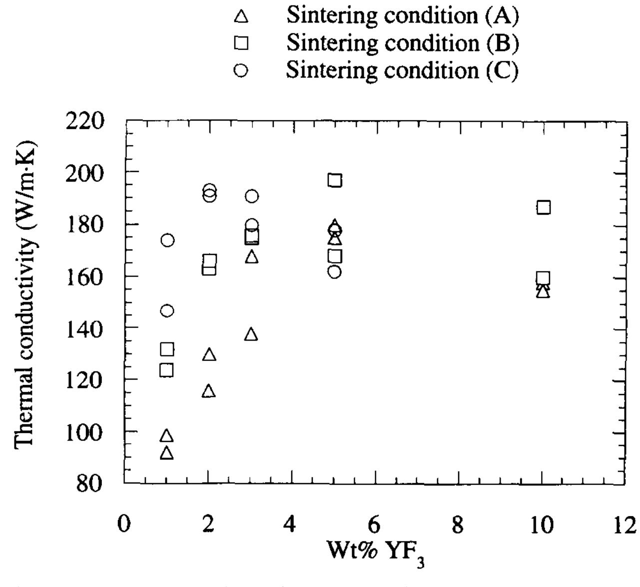

Fig. 6. Thermal conductivity of the AlN samples with added YF_3 and sintered for 6 h at condition A, B and C.

sintering condition A to B to C and (b) the thermal conductivity increases with increasing addition of YF_3 up to about 5 wt%. The decrease in thermal conductivity for the samples with more than 5 wt% YF_3 sintered at condition B and C is most likely due to a decrease in density, see Fig. 3. The oxygen content within the lattice is generally decreasing going from sintering condition A to B to C and decreasing with increasing amounts of YF_3 added, which shows a good correlation between the amount of lattice-dissolved oxygen impurities and the thermal conductivity. This is in accordance with the model proposed by Slack *et al.*[1] and experimental results obtained by others.[9,11,21] However, no correlation between the total amount of oxygen and the thermal conductivity was found. An increasing influence of the secondary phase on the thermal conductivity in the region of very high thermal conductivity (above about 180 W m^{-1} K^{-1}) has been calculated by Buhr and Müller.[11] It is therefore expected to be desirable to be able to remove the secondary phase to obtain a thermal conductivity above about 180 W m^{-1} K^{-1}. This removal can be achieved by choosing proper sintering conditions, e.g. sintering condition C for 6 h. A prolonged reheating at 1900°C in a carbon sagger has previously been used in the literature to remove the Al–Y–O containing secondary phase.[5,8]

On the basis of the results obtained in this work, an optimal sintering programme for AlN with Y-containing additives in a graphite furnace is proposed as follows. The amount of YF_3 added should be below the limit of removing all the Al_2O_3 from the surface of the AlN grains. The reduction of the Al–Y–O containing secondary phase (either by thermal evaporation or reduction with reducing gas species) is kept low during the densification of AlN. This criterion shows the importance of using a powder bed, especially if a graphite furnace is used. In the late part of the sintering, the AlN sample is preferably subjected to a higher partial pressure of reducing species (proposed here to be CO) in order to reduce the secondary phases on the surface of the dense AlN sample, to increase the depletion of oxygen from the AlN lattice and to reduce the amount of secondary phases.

4 Conclusion

Sintering of AlN(YF_3) embedded in AlN powder in a graphite furnace has been studied with respect to reduction of the Al–Y–O containing secondary phases. The secondary phases become more Y-rich (Y_2O_3 or YN) with: (a) increased amounts of YF_3 added, (b) reduced distance between the AlN samples and a graphite source and (c) increased rate of diffusion of gas species (Al_2O, CO and CO_2) through the protective AlN powder bed. When all Al_2O_3 is removed, Y_2O_3 is being reduced to YN. We propose that the mechanism for the reduction of the Al_2O_3 and Y_2O_3 containing secondary phases in AlN specimens sintered in an AlN powder bed is controlled by the diffusion of gas species (CO/CO_2 and/or Al_2O) through the powder bed and the distance between the AlN samples and a graphite source.

The following effects have been observed for increased reduction of the secondary phases: (a) the chemical composition of the secondary phases changes in the order YAG → YAP → YAM → Y_2O_3 → YN; (b) removal of the secondary phases; (c) decreased sinterability of AlN when the amount of YF_3 added increased above 5 wt%; (d) reduction in the lattice oxygen content; and (e) increased thermal conductivity.

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