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Microstructural Development in AlN (YF₃) Ceramics

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Abstract

Microstructural developments in AlN ceramics with added YF₃ as sintering aid have been studied by sintering at 1880°C. In particular, the wetting ability of the secondary phase and the grain growth have been systematically studied by varying the sintering time and the type of embedding of the samples during sintering.

The wetting ability of the Al–Y–O-containing phase on AlN grains was found to be dependent on the content of oxygen impurities on the AlN grain surface. The composition ($Al_5Y_3O_{12}$=YAG, $AlYO_3$=YAP or $Al_2Y_4O_9$=YAM) of the secondary phase and the nitrogen solubility in the Al–Y–O phase seem to have only minor importance for the wetting conditions. The observed grain growth is influenced by the wetting ability of the secondary phase which is determining the contiguity of the samples. From samples showing good wetting, the grain growth mechanism in AlN is determined to be diffusion controlled. In the non-wetting samples, the rate of grain growth is nearly independent of the amount of secondary phase present in the microstructure because the solid–liquid contact area is small. © 1997 Elsevier Science Limited.

1 Introduction

Aluminium nitride (AlN) has attracted much attention over the last ten years especially due to its high thermal conductivity, but other attributes like good dielectric properties, and a thermal expansion coefficient matching that of Si are also important.[1–4] In the literature many papers have focused on how to increase the thermal conductivity.[1–8,10,11,13] The thermal conductivity is found

to be influenced by several factors which can be divided into primary and secondary. The primary factors are material-dependent such as the oxygen content (total and lattice dissolved), the microstructure, lattice defects among others. Secondary factors are the external ones like sintering conditions (graphite, tungsten heating elements or HIP), sintering temperature and time and sintering additives (Y_2O_3, YF_3, CaO,...) to mention some.

AlN has long been considered as a prime candidate for a substrate material for electronic circuits and the main interest for AlN has been to develop a material with high thermal conductivity. However, at the moment there is a growing interest in AlN for other applications. For instance, work has been initiated to test AlN, Al–AlN and AlN–SiC materials as alternative side linings in aluminium production cells.[9] This interest is due to the pure AlN's resistance to molten aluminium and cryolite. It is reasonable to believe that the resistance of AlN to the environment in an aluminium cell depends on the microstructure (i.e. being reduced by the presence of oxide-containing secondary phases on the grain boundaries) as is the case for the thermal conductivity. In general, the production of AlN materials with optimal properties is a demanding task due to the low diffusivity in the solid state in the material. Hence, to achieve excellent properties of AlN, it is important to know how to optimize the secondary factors which in turn influence the primary factors.

Several papers describe how the distribution of the secondary phases changes with the sintering time at constant temperature and composition of the secondary phase.[12–14] Chen *et al.*[13] observed that the secondary phase present after both 2 and 8 h sintering of AlN (2 wt% Y_2O_3) at 1810°C was $Al_5Y_3O_{12}$, but the distribution of this secondary phase was changed from good to non-wetting with increasing sintering time. In this work we have focused on the microstructural development, i.e.

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distribution of Al–Y–O-containing secondary phases and grain growth in AlN sintered with YF_3 additions. The Al–Y–O-containing phases were formed by reactions between the YF_3 and the surface oxide layer on the AlN grains.[10–12]

2 Experimental

Samples of different YF_3 additions from 1 to 10 wt% were fabricated by a slip casting technique and pressureless sintering, following the procedure outlined in previous works.[10,11] AlN powder (Tokuyama Soda, Grade F) and YF_3 (Pennwalt, 99·99% purity) were utilized to prepare the green bodies. An additional series of samples contained 0·5 wt% carbon black (Riedel de Häen) in addition to YF_3. The sample formulations are included in Table 1.

Two different sintering conditions were employed as previously described.[10,11] In sintering condition A the AlN samples were embedded in an AlN powder bed (grain size < 15 μm) in a BN crucible covered by a BN lid (not gas-tight). In sintering condition C the AlN samples were embedded in an AlN powder bed (grain size < 15 μm) in a graphite crucible without a lid. The sintering temperature was 1880°C at both sintering conditions. The sintering time was 2 or 6 h.

The microstructure was investigated by scanning electron microscopy, SEM (Zeiss DSM 940). Secondary phases were analysed by a Teller diffractometer (Phillips PW 1730/10) and EDS (Noran Instruments, Tracor Series II). The AlN surfaces were ground and polished with SiC paper

and diamond powder (6 μm). The samples were finally polished with OP-S SiO_2 suspension (Struers). The polished AlN surfaces were etched in a 20% HF solution (15 s) to reveal the grain boundaries. The polished and etched surfaces were used for determination of the mean grain size. Due to the narrow grain size distribution, about 200 grains were measured for each sample, on at least two different SEM micrographs to reproducibly determine the mean grain size within ± 0·3 μm.[10] The thermal conductivity of the samples was measured to an accuracy within 10% by a laser flash method using a CO_2 laser (Tac 2, 215G).

3 Results and Discussion

The SEM fractographs in Fig. 1 illustrate a general trend observed in this work; the wetting of the AlN grains by the Al–Y–O-containing secondary phase changes with both the sintering conditions and the addition of carbon. The Al–Y–O-containing phases were found to wet the AlN grains only in samples with added YF_3 and sintered in condition A. When 0·5 wt% C was used in combination with YF_3 in sintering condition A, poor wetting of the AlN grains was observed (Fig. 1(b)). Poor wetting was also observed for the samples with added YF_3 and sintered at condition C (Fig. 1(c)). The composition and wetting ability of the secondary phases present in the samples sintered for 2 h are given in Table 1. Al–Y–O-containing phases with similar compositions show different wetting behaviour on

Table 1. AlN sample formulations, sintering conditions and resulting composition of the Al–Y–O-containing secondary phases observed in the bulk and their wetting ability of the AlN grains. The thermal conductivities of the samples are reported. The samples were sintered for 2 h at 1880°C

| Sintering condition	YF_3 addition (wt%)	Secondary phases (bulk)	Wetting ability (visual inspection)	Therm. cond. (W/m K) (±5%)
A	1	YAG[a]	Good	95
A	2	YAG	Good	130
A	3	YAG	Good	160
A	5	YAG, YAP[b]	Good	140
A	10	YAP	Good	140
A	1 + 0·5 wt% C	YAG	Poor	135
A	2 + 0·5 wt% C	YAG	Poor	135
A	3 + 0·5 wt% C	YAG	Poor	137
A	5 + 0·5 wt% C	YAP, YAM[c]	Poor	145
A	10 + 0·5 wt% C	Y_2O_3	Poor	133
C	1	YAG	Poor	130
C	2	YAG, YAM	Poor	145
C	3	YAP, YAM	Poor	180

[a]$Al_5Y_3O_{12}$.
[b]$AlYO_3$.
[c]$Al_2Y_4O_9$.

AlN grains when sintered under different conditions. Hence, from these observations it seems reasonable to state that the composition of the Al–Y–O-containing secondary phase alone has no
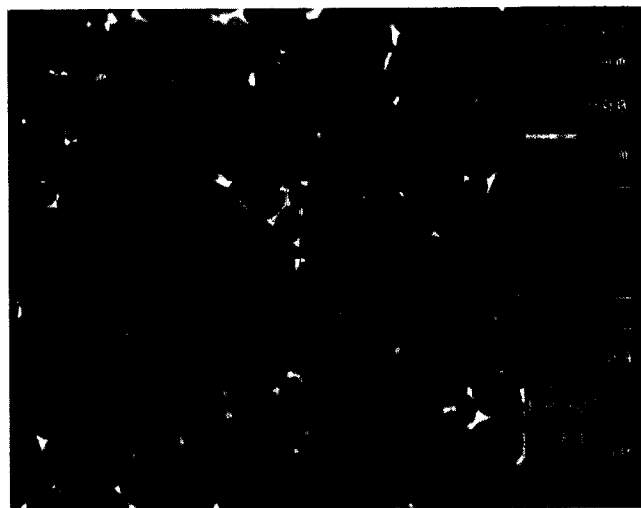
(a)
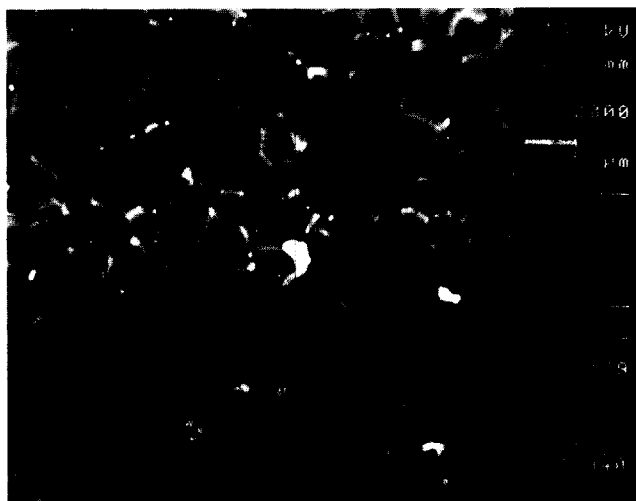
(b)
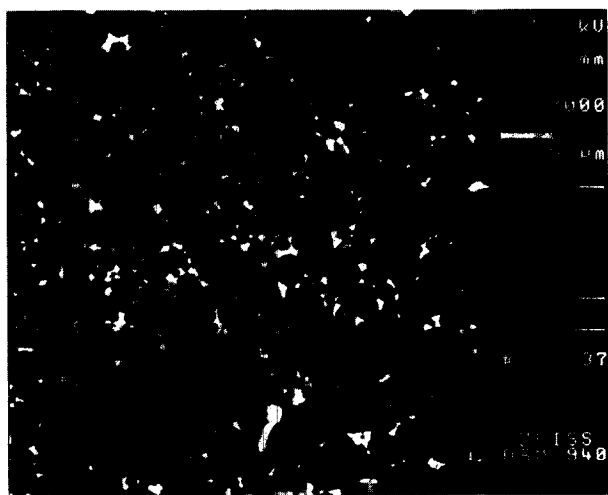
(c)

Fig. 1. SEM fractographs of AlN samples sintered for 2 h at 1880°C (a) 3 wt% YF₃ in condition A, (b) 3 wt% YF₃ + 0·5 wt% C in condition A and (c) 3 wt% YF₃ in condition C.

major effect on its wetting characteristics in AlN ceramics. After 6 h at 1880°C neither the composition nor the wetting characteristics had changed in the samples sintered in condition A. In the samples sintered in condition C, most of the secondary phases were removed from the bulk phase due to reactions involving diffusion of Al_2O from and/or CO to the surface of the AlN sample; this subject is discussed elsewhere.[10,11] However, the fundamentals of wetting are not changed by increased sintering time and therefore references on wetting are to the results observed after 2 h (Fig. 1 and Table 1) in the further discussion. It should also be mentioned that the wetting characteristics discussed were observed at room temperature. During cooling from the sintering temperature the wetting characteristics can possibly change. However we believe that the 'frozen' structures observed give representative information on the wetting behaviour of the Al–Y–O secondary phases on the AlN grains.

The wetting of a solid surface by a liquid depends on the dihedral angle which is given by the energy ratio between the grain boundaries (γ_{ss}) and the liquid-solid surface (γ_{sl}).[15] Large dihedral angle gives poor wetting of the surface. Wetting is associated with a chemical reaction on the surface, and hence aided by the solubility of the solid in the liquid, formation of intermediate compounds and interdiffusion.[15]

In order to investigate the chemical conditions on the AlN grain surface in more detail, EDX analyses were made at points near the secondary phases in the samples shown in Figs 1(a) and (b), see Fig. 2. These samples were chosen because only $Al_5Y_3O_{12}$ was identified as the secondary phase in both samples, but quite different wetting was observed. Clearly, Fig. 2 shows that the oxygen concentration is much higher at the surface of the AlN grains where good wetting by $Al_5Y_3O_{12}$ was observed (sintering condition A). Note that yttrium was not detected at the surface of the AlN grains in the sample in Fig. 1(a) so the observed oxygen is not caused by traces of the secondary phase left on the surface. Wetting is promoted if reactions can take place on the interface between the solid and the liquid. Hence, it seems reasonable that the Al–Y–O-containing phase wets an AlN surface if oxide is present, because γ_{sl} is supposed to be higher for a pure nitride surface than for a AlN surface with oxygen impurities when the liquid is an oxide melt.

The solubility of nitrogen in the Al–Y–O-containing secondary phase depends on the Al/Y ratio according to the Al–Y–O–N phase diagram.[16] The wetting of the AlN grains is observed to be little affected by the chemical composition of
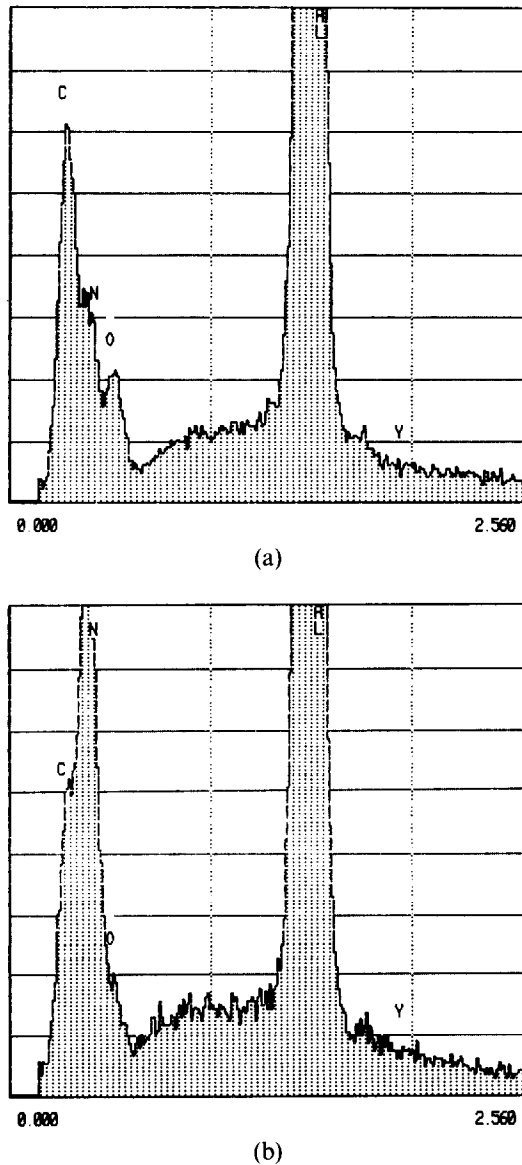
Fig. 2. X-ray microanalysis (spot analysis) on AlN grain surfaces of samples sintered for 2 h in condition A and with (a) 3 wt% YF_3 and (b) 3 wt% YF_3 + 0·5 wt% C.

the Al–Y–O-containing phases. Hence, it seems reasonable that the nitrogen concentration has no significant influence in this concentration range. In previous work,[10] it has been found that the concentration of nitrogen in these Al–Y–O phases is generally low.

The preceding discussion explains why a decreased degree of wetting is observed when less oxygen impurities were present on the AlN grain surface in Fig. 2(b). In a work by Yan et al.,[14] a lower oxygen level on the AlN grain surface was identified when poor wetting was observed (12·6 at%) compared to samples where the Al–Y–O-containing phase wetted the AlN grain surface (21·7 at%). They used Auger emission spectroscopy to measure the average oxygen concentration level on the AlN grain surface. The results in the present work and in the paper by Yan et al.,[14] clearly indicate that the wetting of the Al–Y–O-containing secondary phases is closely related to the

concentration of oxygen on the AlN grain surface. The time-dependent redistribution of secondary phases described in the literature.[12,13] can be understood using this theory. The oxygen level in AlN samples (both on the grain boundaries and in the AlN lattice) is very much influenced by the sintering conditions, especially when performed in a graphite furnace (which is used most frequently). This subject is thoroughly discussed in previous papers.[10,11]

Thermal conductivity is the most frequently reported property of AlN ceramics. The thermal conductivities of the samples sintered for 2 h are included in Table 1. The wetting of the AlN grains by the Al–Y–O phases seems to have no major influence on the thermal conductivity in the range 90–160 W/m K. This seems to be in relatively good agreement with observations made by Buhr and Müller.[8] Other factors influencing the thermal conductivity (e.g. oxygen content) are discussed in several papers.[1–8, 10–13]

Grain growth in liquid phase sintering is generally dependent on particle size distribution, amount of liquid phase (for diffusion-controlled mechanism), contiguity, temperature and time.[15] Hence, the grain growth is also dependent on the wetting properties of the liquid phase, since decreased wetting gives increased contiguity. The grain growth in AlN ceramics is of interest for the mechanical properties of the material as well as for the polishing ability for substrate preparation. However, little information on grain growth exists in the literature.

Table 2 gives the mean grain size measured in the AlN ceramics after 2 and 6 h sintering. All the samples had a density >96% of theoretical except the carbon-containing samples fired for 2 h in condition A. From Table 2, four factors are clearly seen to influence the grain growth (i) the sintering time, (ii) the amount of secondary phase present in the microstructure (i.e. amount of YF_3 added) (iii) the sintering conditions and (iv) the addition of carbon. From the preceding discussion, the secondary factors significantly influence the wetting of the secondary phase and, hence, the contiguity. Models describing a diffusion-controlled grain growth mechanism during liquid phase sintering, predict decreased grain growth with increasing amount of liquid phase present in the microstructure when there is complete wetting of all grains by the liquid phase.[15] The decreased grain growth is due to increased diffusion distance when more liquid phase is present. From the data for sintering condition A when no carbon is added to the samples, the grain growth seems to be diffusion-controlled, see Table 2 and Figs 3(a) and (b). The smaller grains in the samples containing 1

Table 2. Mean grain size for the AlN samples with added YF₃ and sintered at sintering condition A or C for 2 and 6 h

| YF₃ addition | Mean grain size (μm) | | | | | |
| | Condition A | | Condition C | | Condition A + 0·5 wt% C | |
(wt%)	2 h	6 h	2h	6 h	2 h	6 h
1	3·3	5·7	3·4	6·1	2·6	4·6
2	3·8	6·5	3·3	4·8	3·8	5·8
3	4·0	7·4	3·1	3·6	2·2	4·2
5	2·2	3·5	—	—	3·9	4·6
10	2·7	4·2	—	—	2·4	4·6

and 2 wt% YF₃ is supposedly due to too small amounts of secondary phase to obtain complete wetting of all the particle surfaces. However, in the samples with added carbon, the grain size is rather constant after 6 h sintering even though the amount of YF₃ was increased from 1 to 10 wt%. Generally, the Al–Y–O-containing phases wet the

AlN grains poorly in these samples causing a high degree of contiguity. When the wetting is poor there is little difference in the grain growth with increasing amount of secondary phase present because the solid–liquid contact area is small. In the most extreme case for sintering condition C the Al–Y–O-containing secondary phase is almost removed from the bulk after 6 h sintering, see Figs 3(c) and (d). This explains the very limited grain growth observed in the sample with added 3 wt% YF₃ from 2 to 6 h sintering, because solid-state diffusion is rather limited in AlN.
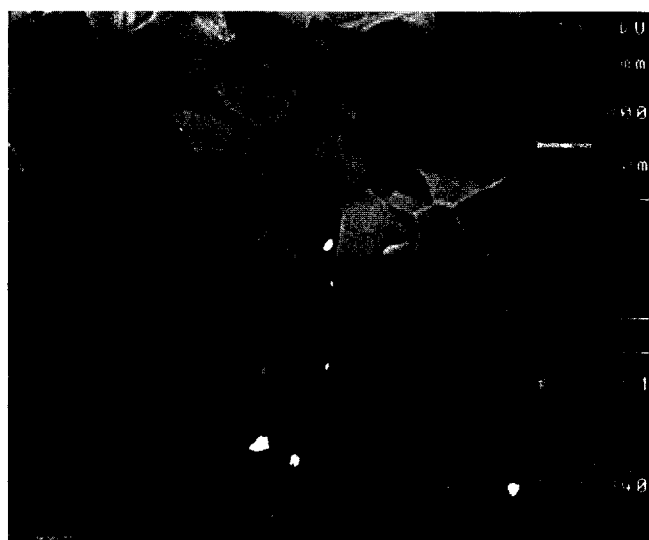
By comparison of the results given in Tables 1 and 2, the mean grain size seems to have no major influence on the thermal conductivity, e.g. the mean grain size measured for the samples sintered in condition A + 0·5 wt% C after 2 h sintering varied from 2·2 to 3·9 μm while the thermal con-
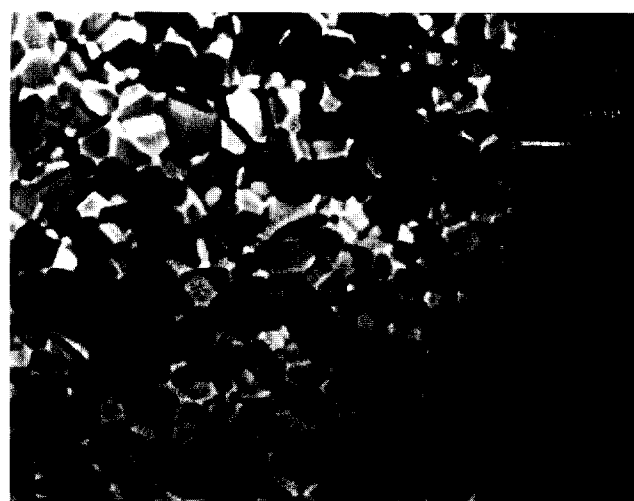

(a)

(b)

(c)

(d)

Fig. 3. SEM fractographs of AlN samples sintered for 6 h (a) 1 wt% YF₃ in condition A, (b) 10 wt% YF₃ in condition A, (c) 1 wt% YF₃ in condition C and (d) 3 wt% YF₃ in condition C.

ductivity was almost constant (135 to 145 W/m K). These results are in accordance with the work done by Watari and Ishizaki,[17] which reports that the thermal conductivity of AlN was unaffected by variation of the grain size in the range from 4 to 40 μm.

4 Conclusions

The wetting of an Al–Y–O-containing phase on AlN grains is associated with the content of oxygen impurities on the AlN grain surface. The wetting is improved with increased concentration of oxygen on the AlN grain surface in contact with the Al–Y–O-containing phase. The composition ($Al_5Y_3O_{12}$, $AlYO_3$ or $Al_2Y_4O_9$) of the Al–Y–O-containing secondary phase and the nitrogen solubility in the Al–Y–O phase seem to have only minor importance for the wetting conditions.

The grain growth is influenced by the wetting conditions which determine the contiguity of the samples. From the samples where the Al–Y–O-containing phase wets the AlN grains, the grain growth mechanism in AlN is determined to be diffusion-controlled. In the non-wetting case, the rate of grain growth is nearly independent of the amount of secondary phase present in the microstructure because the solid–liquid contact area is small.

The distribution of the secondary phases does not seem to have any major influence on the thermal conductivity in the range 90 to 160 W/m K. The thermal conductivity was independent of the mean grain size measured.

References

1. Slack, G. A., Tanzilli, R. A., Pohl, R. O. and Vandersande, J. W., The intrinsic thermal conductivity of AlN. *J. Phys. Chem. Solids*, 1987, **48**, 641–664.
2. Virkar, A. V., Jackson, B. T. and Cutler, R. A., Thermodynamic and kinetic effect of oxygen removal on the thermal conductivity of aluminium nitride. *J. Am. Ceram. Soc.*, 1989, **72**, 2031–2042.
3. Lee, R., Development of high thermal conductivity aluminum nitride ceramics. *J. Am. Ceram. Soc.*, 1991, **74**, 2242–2249.
4. Buhr, H., Müller, G., Wiggers, H., Aldinger, F., Foley, P. and Roosen, A., Phase composition, oxygen and thermal conductivity of AlN(Y$_2$O$_3$) ceramics. *J. Am. Ceram. Soc.*, 1991, **74**, 718–723.
5. Ueno, F. and Horiguchi, A., Grain boundary phase elimination and microstructure of aluminum nitride. In *First Euro-Ceramics*, ed. G. de With, R. A. Terpestra and R. Metselaar. Elsevier Applied Science, 1989, **1**, 1383–1387.
6. Watari, K., Kawamoto, M. and Ishizaki, K., Sintering chemical reactions to increase thermal conductivity of AlN. *J. Matr. Sci.*, 1991, **26**, 4727–4732.
7. Mullot, J., Winter, K., Lecompte, J. P., Müller, G. and Jarrige, J., AlN thermal conductivity of tape casting substrates. In *Third Euro-Ceramics*, ed. P. Duran and J. F. Fernandez. Faenza Editrice Iberica, 1993, **3**, 1027–1031.
8. Buhr, H. and Müller, G., Microstructure and thermal conductivity of AlN(Y$_2$O$_3$) ceramics sintered in different atmospheres. *J. Euro. Ceram. Soc.*, 1993, **12**, 271–277.
9. Skybakmoen, E., SiC-materialer for elektrolyseceller. En kjemisk undersøkelse av kjemisk bestandighet, Presented at the course 'Ildfaste materialer i aluminiumindustrien' 13–14 Nov. Trondheim, Norway, 1995.
10. Hundere, A. M., Sintering of aluminium nitride (AlN) ceramics. Ph.D. Thesis, University of Trondheim, Norway, February 1994.
11. Hundere, A. M. and Einarsrud, M.-A., Effects of reduction of the Al–Y–O-containing secondary phases during sintering of AlN with YF$_3$ additions. *J. Euro. Ceram. Soc.*, 1996, **16**, 899–906.
12. Koestler, C., Bestegen, H., Roosen, A. and Boecker, W., Microstructural development during sintering of AlN ceramics. In *Third Euro-Ceramics*, ed. P. Duran & J. F. Fernandez. Faenza Editrice Iberica, 1993, **3**, 913–918.
13. Chen, C.-F., Perisse, M. E., Ramirez, A. F., Padture, N. P. and Chan, H. M., Effect of grain boundary phase on the thermal conductivity of aluminium nitride ceramic. *J. Matr. Sci.*, 1994, **29**, 1595–1600.
14. Yan, H., Cannon, W. R. and Shanefield, D. J., Evolution of carbon during burnout and sintering of tape-cast aluminum nitride. *J. Am. Ceram. Soc.*, 1993, **76**, 166–172.
15. German, R. M., *Liquid phase sintering*. Plenum Press, New York, 1985.
16. Sun, W., Huang, Z., Tien, T. and Yen, T., Phase relationship in the system Al–Y–O-N. *Matr. Sci. Letter*, 1991, **11**, 67.
17. Watari, K., Ishizaki K. and Fujikawa, T., Thermal conduction mechanism of aluminium nitride ceramics. *J. Matr. Sci.*, 1992, **27**, 2627.