

Preparation and properties of ALCON ($\text{Al}_{28}\text{C}_6\text{O}_{21}\text{N}_6$) ceramics

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The synthesis of $\text{Al}_{28}\text{C}_6\text{O}_{21}\text{N}_6$ powder (ALCON), starting from the binary compounds is described. The powder is resistant to oxidation in air up to 760 °C. From the prepared powder, fully dense ceramics have successfully been prepared using hot pressing. The as-prepared ceramics had a thermal conductivity of $20 \text{ W m}^{-1} \text{ K}^{-1}$. Experiments showed that it is also possible to prepare ALCON ceramics by reactive hot-pressing, starting from Al_2O_3 , AlN and Al_4C_3 . Further optimization is expected to raise the thermal conductivity significantly. The strength, about 300 MPa, is similar to that of AlN. The thermal expansion coefficient of $4.8 \times 10^{-6} \text{ K}^{-1}$ closely matches that of silicon, making application of ALCON ceramics as heat sinks an interesting possibility.

1. Introduction

Materials which combine a high thermal conductivity with a high electrical resistivity at room temperature can be used for heat sinks in microelectronic devices. The best material known with these properties is diamond, but for large-scale application this material is too expensive. Most of the other known materials which possess this combination of properties are compounds which crystallize in a diamond-like structure, e.g. BeO, SiC, c-BN and AlN [1]. BeO is widely used as heat sink but BeO powder is highly toxic and for environmental reasons it is expected to be banished in the near future. Problems are experienced with the electrical conductivity of SiC owing to the relatively low value of the band gap. The cubic form of BN has very attractive properties but preparation and stabilization of this form requires processing in which very high temperatures and pressures are required. The best alternative for BeO at the moment is AlN. A large effort has been made over the last decade to optimize this material, but it is still not widely used. One of the reasons for this is the fact that it is still possible to use BeO. Another reason may be the high price. In some applications in which the thermal conductivity is less critical, alumina substrates are used. The main problem with the use of alumina ceramics as substrate is the thermal mismatch with silicon.

In addition to the binary compounds discussed above, a number of ternary compounds also crystallize in a diamond-related crystal structure. MgSiN_2 crystallizes in an orthorhombic structure, which is derived from the wurtzite structure [2, 3]. Recently, we have reported the preparation of fully dense MgSiN_2 ceramics [4–7]. The maximum thermal conductivity of MgSiN_2 ceramics at room temperature is $25 \text{ W m}^{-1} \text{ K}^{-1}$ [8] which is comparable to the thermal

conductivity of Al_2O_3 ceramics [9]. However, the thermal expansion of MgSiN_2 ceramics ($5.8 \times 10^{-6} \text{ K}^{-1}$) more closely matches that of silicon ($4.8 \times 10^{-6} \text{ K}^{-1}$) than Al_2O_3 ceramics ($7.9 \times 10^{-6} \text{ K}^{-1}$). These data indicate that MgSiN_2 ceramic is a promising heat-sink material, when the thermal conductivity can be increased further [10].

Another ternary compound crystallizing in the diamond-related wurtzite structure is Al_2OC [11]. During our research on the phase system Al_2O_3 – Al_4C_3 –AlN [12], we found a new compound, ALCON ($\text{Al}_{28}\text{C}_6\text{O}_{21}\text{N}_6$) [13], and we expect that ceramics of this material may show a high thermal conductivity because it crystallizes in a diamond-related crystal structure. In this paper we report the synthesis of ALCON starting from the binary compounds and the preparation of ALCON ceramics by hot-pressing. Furthermore, some of the properties of ALCON ceramics are reported.

2. Experimental procedure

Pertinent information about the starting powders used, Al_2O_3 , Al_4C_3 and AlN, are given elsewhere [13]. The powders were mixed in the appropriate ratios in an agate mortar. From the resultant powder mixture, pellets were pressed using a PMMA die at 5 MPa. These pellets were heated in an Astro-C furnace (carbon element) in an argon flow of $200 \text{ cm}^3 \text{ min}^{-1}$ at 1030 mbar. All experiments were done using an h-BN crucible. Prior to heating, the furnace was evacuated twice to about 30 mbar and subsequently filled with argon up to 1030 mbar. The thermocouples used were B₄C–C which were calibrated using a C-type thermocouple. The heating rate was 20 °C min^{-1} to the set point temperature minus 100 °C. A rate of

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10 °C min⁻¹ was used between the aforementioned point and the set point to prevent overshoot. The cooling rate was the maximum available, which is approximately 20 °C min⁻¹ down to 1000 °C. The powder was prepared in two heating cycles with intermediate grinding. In the first cycle the powder was heated for 2 h at 1600 °C, and in the second cycle for 4 h at 1650 °C. The weight loss could be minimized in this way to below 1%.

The fired powder was milled using alumina milling equipment. The particle size distribution of the as-prepared and of the milled powder was measured with a Shimadzu SACP4 centrifugal particle-size analyzer.

The hot-pressing experiments were performed in a hot-press model HP20 of Thermal Technology Ind., using an Astro furnace model 100-4560-FP provided with graphite heating elements. The temperature was measured with a B₄C/C thermocouple. The starting powder (± 10 g) was placed in a graphite die (diameter = 33.7 mm), separated by several graphite foils impregnated with boron nitride powder, in order to obtain several tablets in one run, and closed with a graphite punch. The sintering was performed at a top temperature of 1800 °C and a pressure of 75 MPa for 3 h. The heating and cooling rates were 10 °C min⁻¹. Throughout the whole process the furnace was purged with argon. In a separate experiment, a powder mixture of Al₂O₃, AlN and Al₄C₃, has been hot-pressed using sintering conditions as described above (reactive hot-pressing).

Phase identification was carried out using X-ray diffraction (XRD, Philips PW1800 diffractometer) using monochromatized CuK _{α} radiation. The aluminum content was analyzed using inductively coupled plasma emission spectroscopy (ICP-OES) after dissolving the powder in diluted HCl. The oxygen content was measured using a Leco TC 436 O₂/N₂ analyser and the carbon content was determined using a Strohline Coulomath 702 C/S analyser. Nitrogen was determined as ammonium by ionchromatography after dissolving the powder in diluted HCl. ICP analyses on boron, magnesium, calcium and silicon have been performed to investigate whether these elements are present as contaminants. The density, ρ , of the samples was determined by Archimedes' method. The thermal stability against oxidation of ALCON powder was studied using thermogravimetric analysis (TGA) in flowing oxygen.

The longitudinal wave velocity, v_1 , and the shear wave velocity, v_s , were measured at 10 and 20 MHz, respectively, using the pulse-echo method. From ρ , v_1 and v_s , Young's modulus, E , and Poisson's ratio, ν , were calculated with the usual formula for isotropic materials. No correction for damping was applied because the loss tangent was less than 0.05 [14]. The standard deviation in Young's modulus was estimated to be about 2 GPa. The Vickers hardness, H_v , was measured on a polished specimen. A load of 20 N was applied for about 15 s. The average sample standard deviation using five readings was about 1.6 GPa. The fracture toughness, K_{Ic} , was measured in a dry nitrogen gas atmosphere (≈ 200 p.p.m. V H₂O) with the three-point bend test (span 12 mm, crosshead speed

0.1 min min⁻¹) using a specimen measuring $1 \times 3 \times 15$ mm³. A notch with a relative depth of about 0.15 and a width of 100 μ m was sawn into the specimen. Pre-cracking was done by a Knoop indentation (10 N load) at the notch root on both sides of the specimen. The compliance factor was calculated as described elsewhere [15]. The small type of specimen makes efficient use of the available material while retaining reliability and accuracy [16]. Five specimens were used for the K_{Ic} determination, resulting in an average sample standard deviation of 0.1 MPa m^{1/2}. The strength was measured in the same bending apparatus. Samples were sawn with a 100 μ m diamond wheel. Again, five specimens were used, resulting in a simple standard deviation of 20 MPa.

Thermal diffusivity measurements were carried out using a laserflash method, which is described in detail by Sölter *et al.* [17]. The C_p was measured using a Perkin-Elmer DSC7 calorimeter. The thermal expansion coefficient was determined in nitrogen temperature range 20–600 °C using a specimen of 1 cm length in a dual-rod dilatometer (Netsch). As a reference, a fused silica sample with an expansion coefficient of 0.55×10^{-6} K⁻¹ was used. The bandgap for ALCON at room temperature was estimated from diffuse reflectance spectra.

3. Results

The reacted powder was white. An X-ray diffraction pattern of the prepared powder is presented in Fig. 1a. All lines can be indexed using the unit-cell of ALCON as reported previously [13]: rhombohedral structure (R-3m, no. 166): $a = 0.5456$ nm and $c = 1.4956$ nm (hexagonal description) or $a = 0.5897$ nm and $\alpha = 55.11^\circ$ (rhombohedral description).

Particle-size analyses of the prepared powder dispersed in ethanol showed the existence of relatively large particles and agglomerates. Therefore, the powder was milled in hexane to obtain a narrower range in the particle-size distribution. After 6 h milling, a smaller particle-size distribution was obtained. The particle-size distributions before and after milling are presented in Fig. 2: Note that the as-prepared powder also contained a fraction of large particles (> 20 μ m) which cannot be measured with the technique used.

Hot-pressing experiments were performed at various temperatures. The conditions and the corresponding sample codes are presented in Table I. During the hot-pressing experiments, the dilation of the sample was measured. The measured data indicate that densification of ALCON starts at 1600 °C. The prepared ceramics are a dark grey colour. The X-ray diffraction pattern of a ceramic sample (HP4) is shown in Fig. 1b. The X-ray diffraction pattern of the reactive hot-pressed sample, which has been prepared starting from Al₂O₃, AlN and Al₄C₃ powder (sample HP7) is presented in Fig. 1c. This sample contains about 5% Al₂O₃ as a second phase. However, this experiment shows clearly that it is possible to prepare ALCON ceramics by reactive sintering.

The densities of the different samples are also presented in Table I. No relative densities can be given

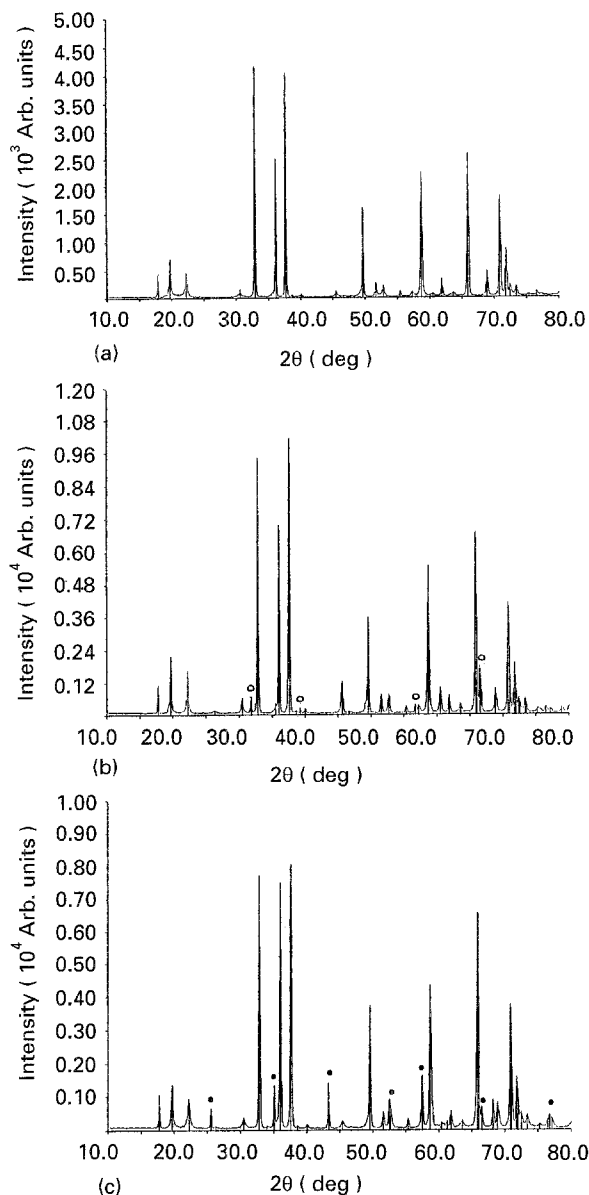


Figure 1 X-ray diffraction patterns of (a) the prepared ALCON powder, (b) the hot-pressed sample HP4 and (c) the sample prepared by reactive hot pressing. (○), Alon; (●), Al_2O_3 .

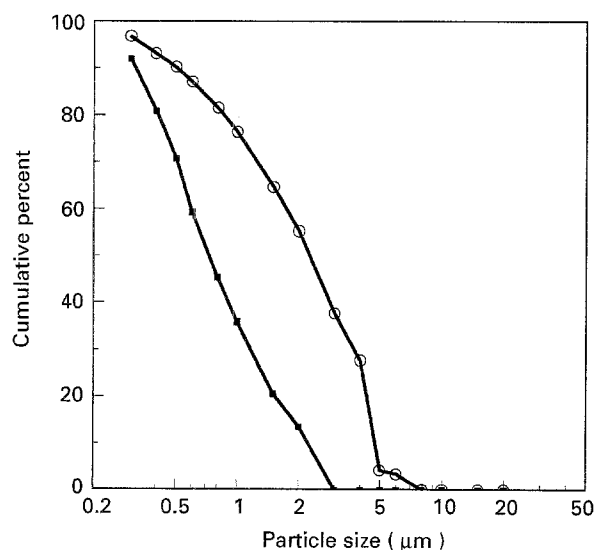


Figure 2 Particle-size distributions (○) before and (■) after 6 h milling.

because the theoretical density of ALCON cannot be calculated because the exact crystal structure is not yet known. However, the density of the powder was measured using krypton pycnometry. The density found with pycnometry was $3.11(5) \text{ g cm}^{-3}$. However, the density can also be calculated from the molecular formula and the lattice parameters when some assumptions are made:

(a) Carbon, oxygen, nitrogen on anion sites aluminium and vacancies on cation sites ($[\text{Al}_{28}\text{V}_7]$ - $[\text{C}_6\text{O}_{21}\text{N}_6]$): $\rightarrow 2.94 \text{ g cm}^{-3}$

(b) almost stoichiometric, no vacancies, carbon distributed over cation anion sites ($\approx [\text{Al}_{28}\text{C}_3]$ - $[\text{C}_3\text{O}_{21}\text{N}_6]$): $\rightarrow 3.13 \text{ g cm}^{-3}$.

The value found with krypton pycnometry agrees best with the stoichiometric model (b) in which no vacancies are present in the crystal structure.

The results of the chemical analyses on sample HP4 are presented in Table II. The results are in good agreement with the theoretical values. The total amount of weight percentages of $\text{Al} + \text{O} + \text{C} + \text{N}$ is close to 100%. This result is not unsatisfactory, taking the errors into account.

The grains sizes and the morphology of the second phases of the sintered samples have been examined using a scanning electron microscope (SEM). In Fig. 3, scanning electron micrographs are shown of a fractured sample at different magnifications. The micrographs indicate that full density has been achieved. Furthermore, it is shown clearly that the fracture occurs through the grains and not along the grain boundaries.

The thermal diffusivities, λ , measured are 0.079, 0.066, $0.086 \text{ cm}^2 \text{ s}^{-1}$, respectively, for samples HP1, HP2 and HP4, at 35°C . From these values the thermal conductivities, κ , can be calculated using

$$\kappa = \lambda \rho C_p \quad (1)$$

Using the measured C_p value of ALCON of $0.78 \text{ J kg}^{-1} \text{ K}^{-1}$ (also at 35°C) and the measured density, d , the thermal conductivities are estimated to be 19, 15 and $20 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, for samples HP1, HP2 and HP4, at 35°C . On samples HP3 and HP5 the thermal diffusivity could not be measured reliably, probably due to microcracks in the pellets. The thermal diffusivity of the reactive hot-pressed sample, HP7, is $0.076 \text{ cm}^2 \text{ s}^{-1}$ which results in a thermal conductivity of $18 \text{ W m}^{-1} \text{ K}^{-1}$.

In ALCON, a large number of parallel, but aperiodically spaced, planar defects has been observed with high-resolution electron microscopy [12]. To investigate the influence of these defects on the thermal conductivity, a sample (HP4) was heated at a temperature of 1550°C for 2 h in argon and slowly cooled to room temperature with a rate of 2°C min^{-1} . The temperature of 1550°C was chosen because this is the minimum temperature at which ALCON is formed [12]. The thermal conductivity of the sample after this annealing step is still $20 \text{ W m}^{-1} \text{ K}^{-1}$. So the influence of the cooling rate on the thermal conductivity of ALCON is small.

TABLE I Densities and X-ray diffraction (XRD) results of the hot-pressed ALCON ceramics

Sample	Hot-pressing (h) (°C)	Density (g cm ⁻³)	XRD; other phases
HP1	1/2 1825	3.019	Alon (≈ 10%), mon (≈ 5%)
HP2	3 1800	2.997	Alon (< 5%), trace mon
HP3	3 1750	3.009	Al ₂ O ₃ (≈ 10%)
HP4	3 1800	2.972	Alon (< 5%)
HP5	3 1800	2.990	Alon (< 5%)
HP7 ^a	3 1800	3.040	Al ₂ O ₃ (≈ 5%–10%)

^aSample HP7 was prepared by reactive hot pressing starting from Al₂O₃, AlN and Al₄C₃ powder.

TABLE II Results of the elemental analyses (wt %) on sample HP4

Sample	Al	O	C	N	Total (%)
Theoretical	60.6	26.9	5.8	6.7	100
HP4	59.0	28.1	5.4	7.1	99.6

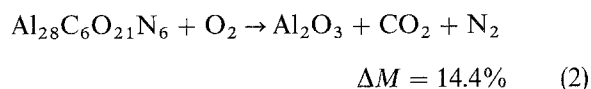
wt % Al: 3% error
wt % O, wt % C, wt % N: 5% error

The thermal expansion of a ceramic sample as a function of temperature has been measured in nitrogen. The thermal expansion coefficient, α , over the temperature range from 20–600 °C was measured to be $4.8 \times 10^{-6} \text{ K}^{-1}$. It is of interest to note that the same thermal expansion coefficient has been reported for AlN [18].

The optical band gap was calculated from diffuse reflectance spectra on powders. The spectra were made using a Perkin-Elmer Lambda 19 spectrometer

equipped with an integrating sphere. The optical band gap was taken as the energy at the point of 50% reflection. The bandgap for ALCON at room temperature was calculated to be 3.9 eV from diffuse reflectance spectra.

Thermogravimetric analysis (TGA) was performed on ALCON powder in flowing oxygen to investigate when oxidation starts. For comparison, the oxidation of AlN powder was also investigated. Fig. 4 shows the TGA diagram of ALCON and AlN. Oxidation of ALCON starts at 760 °C while oxidation of AlN starts at about 840 °C. The weight increase can be calculated from



The observed weight increase is 14.0% which is in good agreement with the calculated value. X-ray powder diffraction on the oxidized powder indicated that

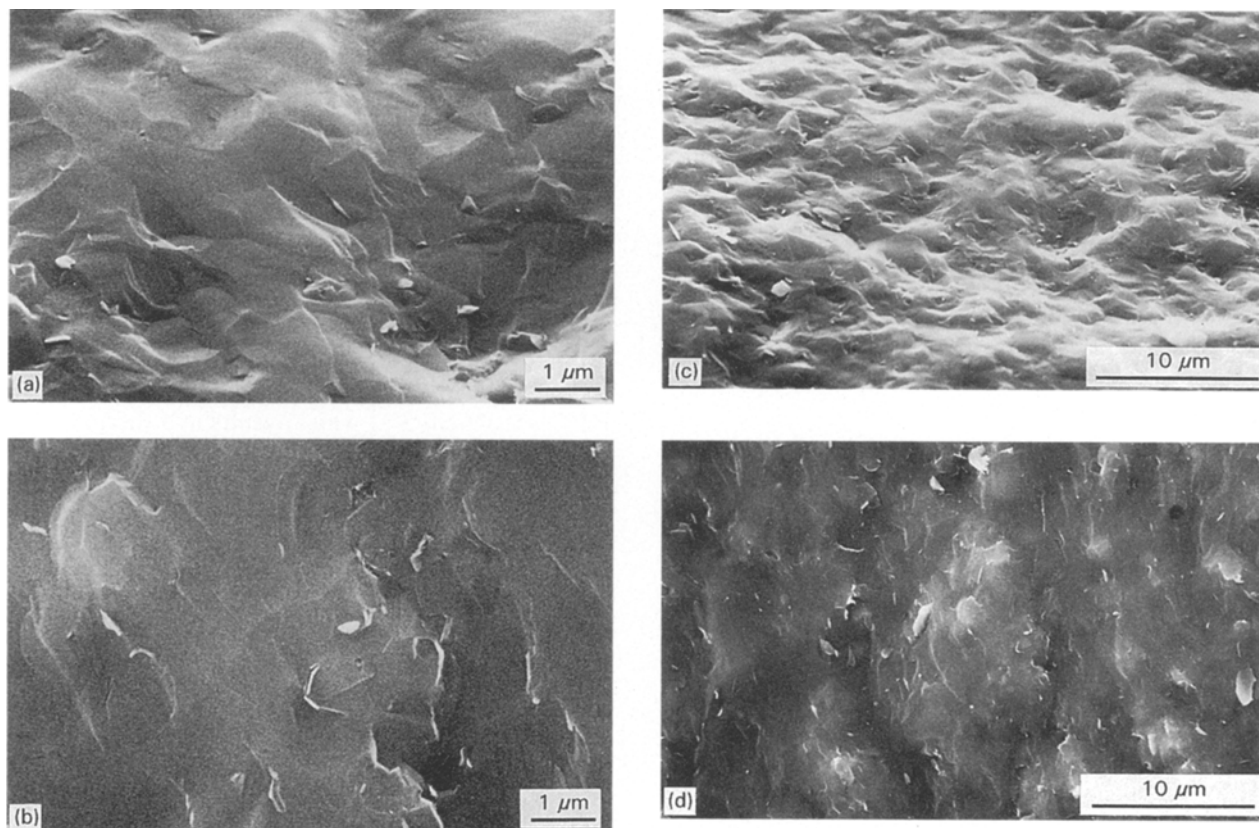


Figure 3 Scanning electron micrographs of a fractured sample at different magnifications.

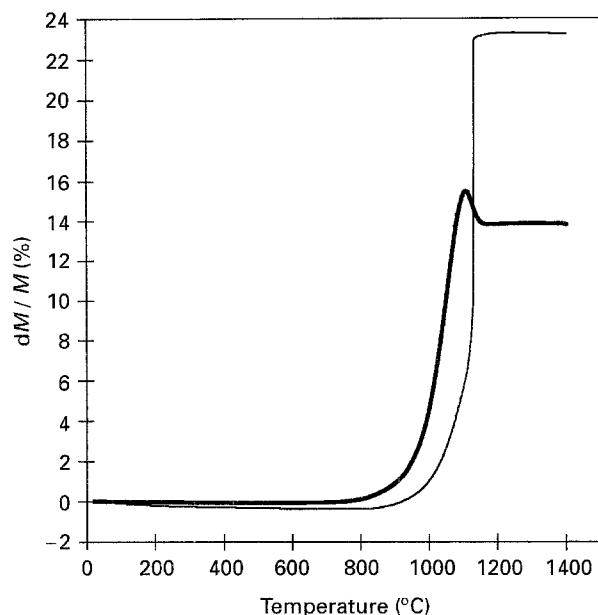


Figure 4 The TGA diagram of (—) ALCON and (---) AlN as measured in flowing oxygen.

alumina is left as the only compound. The observed weight increase for AlN is 23.5% which is lower than the calculated value of 24.4%. This difference is due to the fact that the AlN powder is not pure but contains about 1 wt% oxygen.

The results for the measurements of the hardness, H_v , the fracture toughness, K_{Ic} , and the strength, σ , are presented in Table III. The elastic properties are also presented in Table III. For comparison, the reported mechanical properties of CaSiN_2 , MgSiN_2 , AlN and Al_2O_3 are also presented.

4. Discussion

The thermal conductivity of this new material is already comparable to that of alumina but still significantly lower than for AlN ceramics. It should be remembered that in the case of AlN ceramics, an enormous effort has been made over the last decade to arrive at a thermal conductivity above $150 \text{ W m}^{-1} \text{ K}^{-1}$ [23, 24]. In the present case, the pre-

sented value is that observed for non-optimized material. Furthermore, the X-ray diffraction pattern indicates that the hot-pressed sample HP4 contained about 5% second phases. At the moment it is uncertain how the second phases are distributed. When the second phases are distributed between the grains it is known from work on AlN ceramics that the thermal conductivity can be decreased by a factor of 4. However, when the second phases are located at triple points, the influence of the second phases on the thermal conductivity is low. More detailed microstructural investigations must be made to reveal the distribution of second phases.

The simplified thermal conductivity model as described elsewhere [10], using the phenomenological data as described below, yields a κ of $120 \text{ W m}^{-1} \text{ K}^{-1}$ at $T = 300 \text{ K}$. This value is much higher than the observed value, so considerable improvement of the thermal conductivity is expected when improved processing conditions, well within reach, are realized. It should be recalled that for MgSiN_2 , the model [10] yields a κ -value of $120 \text{ W m}^{-1} \text{ K}^{-1}$ at $T = 300 \text{ K}$. Originally, for hot-pressed MgSiN_2 ceramics with a relative density of 99.5% a thermal conductivity of $15 \text{ W m}^{-1} \text{ K}^{-1}$ has been reported [5]. Preliminary optimization experiments on hot-pressed MgSiN_2 ceramics have already resulted in a thermal conductivity of $25 \text{ W m}^{-1} \text{ K}^{-1}$ [8].

The hardness of ALCON is somewhat lower than for Al_2O_3 but higher than for AlN, MgSiN_2 and CaSiN_2 . The fracture toughness of ALCON is significantly lower than for the other materials in Table III. Because the Young's modulus is comparable, the fracture energy, $J = K_{Ic}^2(1 - \nu^2)/2E$, for ALCON is rather low, about 5 J m^{-2} as compared with approximately 40 J m^{-2} for MgSiN_2 . On the other hand, its strength is already comparable to AlN and MgSiN_2 . An estimate can be made of the flaw size, $a = (K_{Ic}/Y\sigma)^2$, using the compliance factor $Y = 1.26$, when we assume that the critical flaws are half-penny shaped surface defects. These defect sizes are also given in Table III. For ALCON, $a = 19 \mu\text{m}$, about five times the average grain size. A similar estimate for MgSiN_2 yields $a = 167 \mu\text{m}$, about 80 times the average grain

TABLE III Mechanical and elastic properties of ALCON ceramics. The standard deviation and the number of measurements used are given in parentheses. The properties for MgSiN_2 , CaSiN_2 , AlN and Al_2O_3 are also presented for comparison. The characteristic parameters, R and R' , for the thermal shock resistance of ceramics, the critical flaw size, a , and the fracture energy, J , are also presented

	ALCON	CaSiN_2	MgSiN_2	Al_2O_3	AlN
H_v (GPa)	14.0 (0.9, 4)	9.6 [18]	14.2 [4]	19.5 [9]	12 [19]
K_{Ic} ($\text{MPa m}^{1/2}$)	1.62 (0.07, 7)	2.1 [18]	4.4 [4]	4–5 [9]	2.7 [20]
σ (MPa)	295	179 [18]	270 [6]	450 [19]	340 [19]
E (GPa)	239	174 [18]	235 [6]	398 [9]	315 [21]
ν	0.256	0.255 [18]	0.232 [6]	0.235 [9]	0.245 [9]
α (10^{-6} K^{-1}) ^a	4.8	7.6 [18]	5.8 [6]	7.9 [19]	4.8 [22]
k ($\text{W m}^{-1} \text{ K}^{-1}$)	21	2.4 [18]	17 [6]	20 [9]	150 [23]
R (K)	190	100	150	110	170
R' (kW m^{-1})	4.0	0.24	2.5	2.2	25
a (μm)	19	87	167	63	40
J (J m^{-2})	5	12	39	24	11

^a As measured between 20 and 600 °C.

size. Fractography of the ALCON strength specimens revealed that the critical defects were large grains, isolated pores and machining damage of a size similar to the calculated average one. The high value for the strength of ALCON is probably due to both the powder preparation and hot-pressing. This indicates there is little room for improvement in the processing with respect to the mechanical behaviour, in contrast to the situation with MgSiN₂.

The thermal shock resistance of ceramics can be conveniently characterized by the parameters $R = \sigma(1 - \nu) / E\alpha$ and $R' = kR$, where the symbols have the meaning as defined earlier. The parameter R characterizes the materials resistance towards thermal shock for high heat-transfer conditions. The parameter R' does the same, but for mild heat-transfer conditions. From the experimental data, the parameters R and R' are calculated and given in Table III. For comparison, the values as calculated for AlN, MgSiN₂ and Al₂O₃ are also indicated. From this table it can be concluded that the thermal shock resistance, R , of ALCON is nearly twice that of Al₂O₃ and as good as for AlN. For mild heat-transfer conditions, the thermal shock resistance, R' , of ALCON is again twice that of Al₂O₃, but not as good as AlN, because of the much higher thermal conductivity of AlN.

5. Conclusion

The synthesis of Al₂₈C₆O₂₁N₆ powder, ALCON, starting from the binary compounds has been reported. This powder is resistant to oxidation in air up to 760°C. From the prepared powder, fully dense ceramics have successfully been prepared using hot-pressing. The as-prepared ceramics had a thermal conductivity of 20 W m⁻¹ K⁻¹. Experiments showed that it is also possible to prepare ALCON ceramics by reactive hot-pressing starting from Al₂O₃, AlN and Al₄C₃. Further optimization is expected to raise the thermal conductivity significantly. The strength, about 300 MPa, is similar to that of AlN. The thermal expansion coefficient of 4.8 × 10⁻⁶ K⁻¹ closely matches that of silicon, making application of ALCON ceramics as heat sinks an interesting possibility.

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