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Aluminium nitride ceramics prepared by a pyrolytic route

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Metallic aluminium was dissolved in a fluid organic electrolyte. Drying of the viscous solution obtained, by simply evaporating the organic compounds, resulted in a relatively coarse powder with a broad particle size distribution. By contrast, a very fine-grained powder with a mean particle size in the submicrometre range, was obtained by hot-paraffin drying of a precursor solution of controlled viscosity. Sintering experiments with hot-paraffin dried powders calcined in ammonia, showed that these powders can be densified at 1820 °C without sintering additives, to densities of $>$ 99% theoretical density.

1. Introduction

In the last few years, aluminium nitride has generated a great deal of interest, predominantly due to its potential use as material for high and ultra-high integrated circuit carriers [1]. However, other applications include evaporation boats or crucibles for molten metals. Recently, Japanese manufacturers have introduced components for engineering applications with remarkable tooling and machining properties [2]. The predominant properties of aluminium nitride ceramics are their high thermal conductivity (theoretical value 320 $W\,m^{-1}\,K^{-1}$), their high ohmic resistance, their high mechanical strength and their low wettability by molten metals.

Conventional synthesis routes for aluminium nitride are the direct nitridation of metallic aluminium [3] and the carbothermic reaction of alumina, carbon and nitrogen [4]. In addition to these two routes, the gas-phase reaction of aluminium chloride and ammonia has been used for the preparation of aluminium nitride, in recent years [5]. All these synthesis routes are high-temperature processes, and the powders obtained have large crystallite sizes and hence low sinterability. Generally, aluminium nitride powders produced by high-temperature routes cannot be densified without pressure and sintering aids.

By contrast, synthesis routes which allow lower formation temperatures, enable the production of powders with smaller crystallite sizes. In principle, these powders might be densified without pressure and sintering aids. In the last few years, pyrolytic routes which yield aluminium nitride have been investigated. As starting materials, aluminium hydride, AlH_3 [6, 7], or aluminium alkyles, AlR_3 [8], were predominantly used. By the addition of ammonia or organic amines, oligomeric or polymeric compounds, such as polyiminoalanes, $1/n\,[AlH(NR)]_n$, are formed. During calcining of these intermediates, organic compounds are evaporated and aluminium nitride is formed. To achieve sufficient yields, highly polymeric intermediates are required. Other synthesis routes, previously mentioned in the literature, are a route via aluminium triazide [9], the reaction of alkali amides with aluminium halides or metallic aluminium [9], and the reaction of organic amines with metallic aluminium under high pressure [10]. It should be mentioned that all these routes require high technical expenditure, in some cases relatively expensive starting materials, and often result in insufficient ceramic yields. This paper provides a study of the preparation of aluminium nitride ceramics by a low-cost synthesis route, using a polymeric precursor.

2. Preparation and properties of the polymeric precursor

Metallic aluminium was anodically dissolved in an organic electrolyte consisting of acetonitrile which acted as a solvent, *n*-propylamine and tetraalkylammonium bromide as a supporting electrolyte. The latter was required to achieve a sufficient ionic conductivity of the electrolyte, necessary to reduce ohmic drops. A double-walled glass vessel contained the electrodes and the electrolyte (see Fig. 1). Cathodes and anodes were both formed by sheets of metallic aluminium (thickness 1 mm); the distance between two electrodes was also 1 mm. The electrodes were alternately connected to a thick aluminium wire inserted from the top for the power supply. The polarity of the electrodes was inverted every 15 min to achieve a homogeneous dissolution of all electrodes. At the top of the vessel a condenser recovered solvent and amine, which were vapourized or carried along with the gas stream. The electrolysis was carried out at a voltage of 5–6 V and a current of about 40 A. The current remained almost constant over a period of about 4 h, and then decreased, due to increasing viscosity of the solution. The electrolysis was then stopped, and the electrolyte drawn off to another vessel. The experimental details have already been discussed elsewhere [11, 12].

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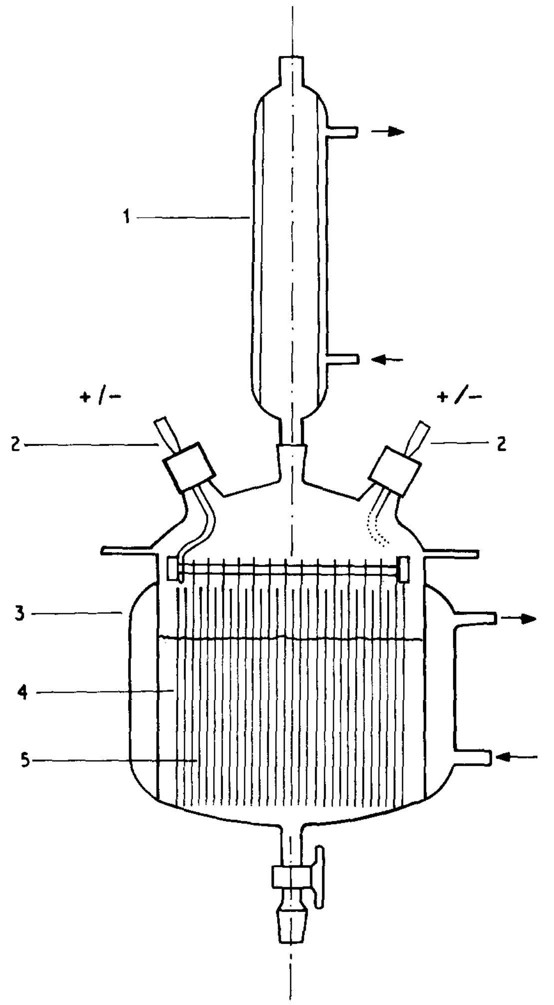


Figure 1 Schematic drawing of the apparatus. 1, condenser; 2, wires for the power supply; 3, double walled glass vessel; 4, electrolyte; 5, aluminium electrodes.

The reaction mechanism suggested is as follows.

Anodic reaction

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\,\mathrm{e}^- \tag{1}$$

Cathodic reaction

$$3\,\mathrm{NH_2R} + 3\,\mathrm{e}^- \rightarrow 3\,\mathrm{NHR}^- + 3/2\,\mathrm{H_2} \tag{2}$$

$$3\,\mathrm{NH_2R} + \mathrm{Al} \rightarrow \mathrm{Al(NHR)_3} + 3/2\,\mathrm{H_2} \tag{3}$$

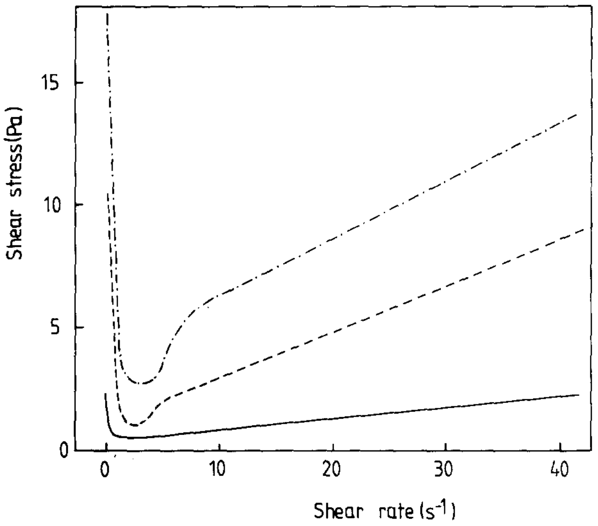


Figure 2 Flow diagram of the polymeric precursor solution, diluted with different amounts of propylamine. (–·–) 23 vol %, (– – –) 30 vol %, (———) 40 vol %.

At the anode, metallic aluminium is oxidized, at the cathode, propylamine is reduced, and the corresponding anion and gaseous hydrogen (gas bubbles) are formed. As an intermediate, the monomeric aminoalane $\mathrm{Al(NHR)_3}$ can be assumed.

After electrolysis, the vessel was evacuated in order to remove solvent and excess amine. At first, a highly viscous liquid was obtained; further heating led to a gel-like consistency and finally, a polymeric foam full of gas bubbles was formed.

To characterize the precursor solutions, flow curves (Brookfield Digital Viscosimeter DV-II) and Fourier transform-infrared (FTIR) spectra (Mattson Instruments, Polaris) were recorded. The highly viscous solution obtained after an electrolysis time of 2.5 h was diluted with different quantities (23, 30 and 40 vol %) of *n*-propylamine. The flow behaviour (see Fig. 2) was strongly non-Newtonian. At a shear rate of 0.2 s^{-1}, a rather high shear stress was observed, which decreased when the shear rate was lowered. Further increasing the shear rate resulted in an increase of the shear stress. The virtual viscosity of another series of experiments, calculated from shear stress (20 s^{-1}) and shear rate, is shown in Fig. 3 as a function of the shear

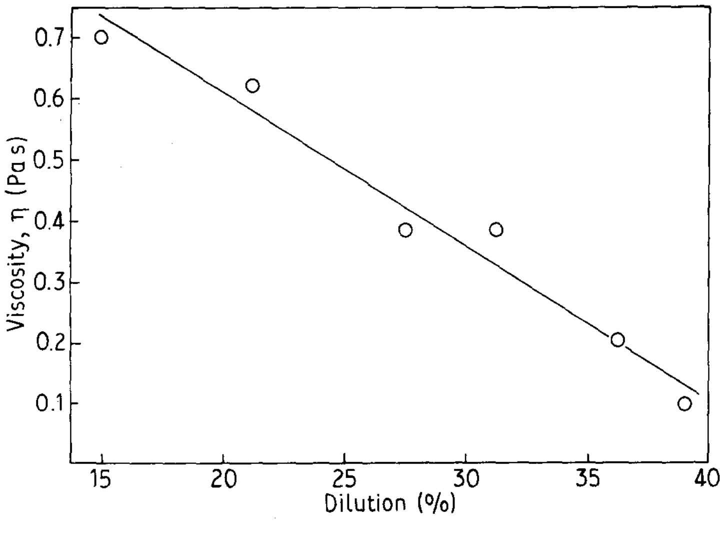
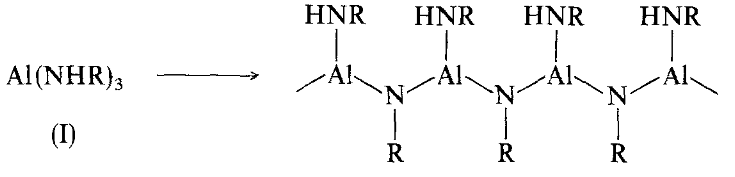


Figure 3 Virtual viscosity, calculated from shear rate (20 s^{-1}) and shear stress of a polymeric precursor solution diluted with different amounts of propylamine.

rate, for precursor solutions diluted with different amounts of propylamine. The virtual viscosity of the solution depended strongly on the amount of *n*-propylamine added to the initial solution and varied over nearly one order of magnitude, if the concentration of *n*-propylamine was increased from 21 to 38 vol %. This emphasizes the necessity of controlled concentrations, to achieve reproducible rheological behaviour during subsequent treatment.

Fig. 4 shows a FTIR spectrum of the precursor dried at 250 °C. Strong absorptions both in the region at about 3300–3500 $\mathrm{cm^{-1}}$ and at about 1600 $\mathrm{cm^{-1}}$ indicated that considerable numbers of N–H bonds were still present. C–H bonds can be seen at 2850–2950 and 1370–1470 $\mathrm{cm^{-1}}$. The absorption at about 2100 $\mathrm{cm^{-1}}$ may be due to Al–H bonds. The broad absorption in the region at 500–1000 $\mathrm{cm^{-1}}$ is predominantly due to Al–N bonds. X-ray diffraction (XRD) patterns show the dried precursor to be completely amorphous.

All these experiments prove that the monomeric intermediate, $\mathrm{Al(NHR)_3}$, polycondenses to a highly polymeric product. The following reactions can be assumed



(II)

(4)

$$\xrightarrow{\qquad} \mathrm{Al(NR)_{1.5}}$$

(III)

(5)

Compound II corresponds to a one-dimensionally polycondensed product, which might further polycondense to the three-dimensionally polycondensed Compound III. CHN analysis of the dried precursor resulted in an empirical formula of $\mathrm{AlC_{5.5}H_{12.6}N_{1.43}}$, while Compound III may be written as $\mathrm{AlC_{4.5}H_{10.5}N_{1.5}}$. The disagreement in the empirical formulae, as well as the occurrence of Al–H bonds, highlights that the reaction mechanism is much more complicated than the description given by reactions 1–5.

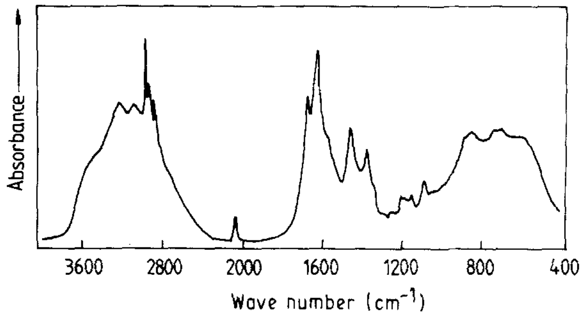


Figure 4 FTIR spectra of the polymeric precursor dried at 250 °C.

3. Drying and calcining of the polymeric precursor

In order to study the chemistry of the calcination process, the precursor solution was dried by attaching a vacuum pump to the vessel and subsequently heating it. During thermal treatment of the dried precursor, neither the occurrence of any organic liquid phase, nor any melting of the organometallic compound, was observed. This is in contrast to most polysilane or polycarbosilane precursors, and facilitates powder processing because, in many cases, the morphology and the mean grain size are not drastically affected by the calcination procedure. However, it should be noted that a precursor which does not melt during thermal treatment, cannot be used for the melt spinning of fibres. Direct fibre spinning from the precursor solution may be applicable.

Fig. 5 shows a thermogravimetric analysis (TGA) profile of the polymeric precursor. The main weight loss occurred up to a temperature of 200 °C, then the slope decreased and, at temperatures higher than 550 °C, no further weight loss occurred. Calcining the precursor at temperatures higher than 750 °C led to the formation of microcrystalline AlN. At a calcination temperature of 850 °C, using X-ray line broadening and the Scherrer equation, a mean crystallite size of about 20 nm was calculated. Fig. 6 shows XRD patterns of samples calcined in different atmospheres. Powders calcined in a nitrogen atmosphere show slightly more pronounced line broadening than those calcined in an ammonia atmosphere. Powders calcined at 1000 °C in nitrogen/hydrogen gas mixtures (3% $\mathrm{H_2}$) show a quite different behaviour: very broad lines are superimposed by very sharp lines. A bimodal distribution of the crystallite sizes can be assumed. Figs 7 and 8 show scanning electron micrographs of samples calcined in ammonia and nitrogen/hydrogen atmospheres, respectively. Both powders are quite coarse. In Fig. 8, the particle is quite inhomogeneous: its upper part has a fairly similar shape to those which can be observed if the powder has been calcined in an ammonia atmosphere; the lower part shows some very regular crystals. As shown in the XRD patterns, no additional phase such as oxynitrides were observed, these crystals also consisted of AlN and should be related to the very narrow lines in the XRD patterns. The upper part of the particle in Fig. 8 should be related to the broadened peaks. It might be assumed

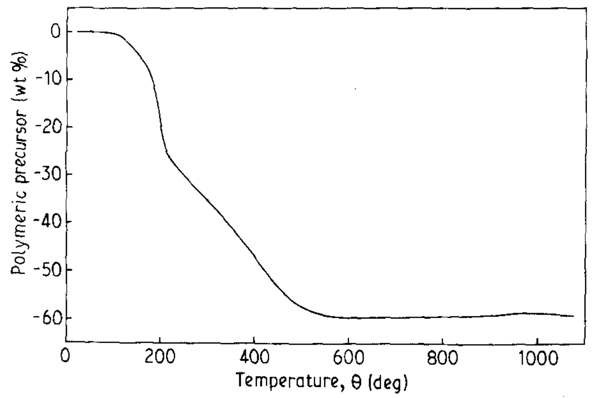


Figure 5 TGA profile of the dried polymeric precursor.

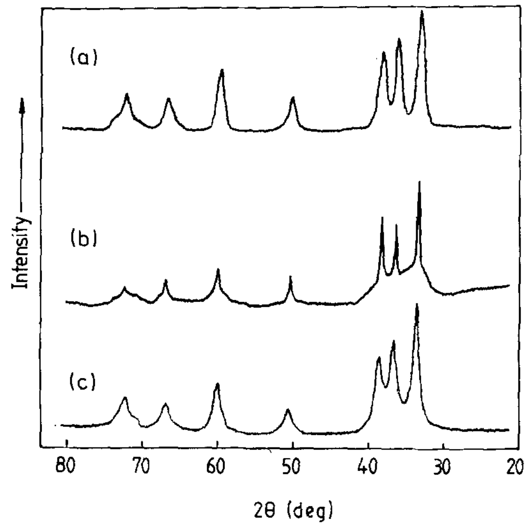


Figure 6 XRD patterns of products calcined at 1000 °C in (a) NH_3, (b) N_2/H_2, and (c) N_2 atmospheres.

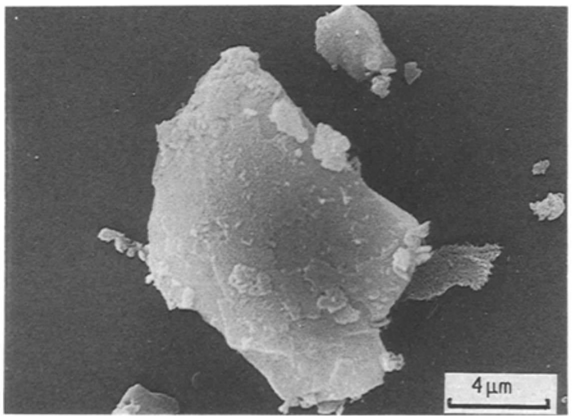


Figure 7 Scanning electron micrograph of a powder dried by attaching a vacuum pump to the vessel containing the precursor solution, and subsequently heating the vessel (calcined in ammonia at 900 °C).

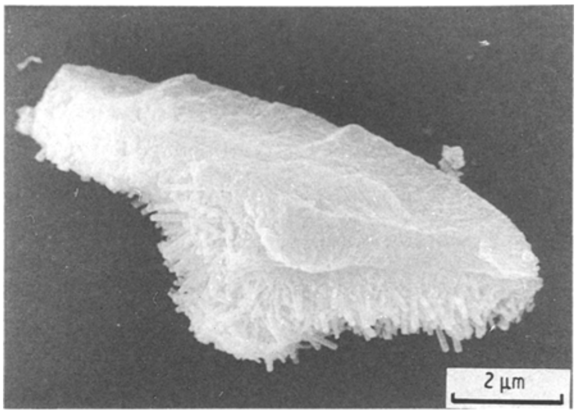


Figure 8 Scanning electron micrograph of a powder dried by attaching a vacuum pump to the vessel containing the precursor solution, and subsequently heating the vessel (calcined in a N_2/H_2 atmosphere at 900 °C).

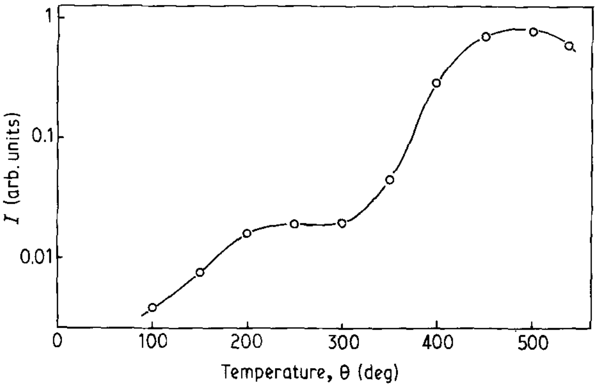


Figure 9 Intensity of the ESR signal at $g = 1.99$ (peak-to-peak) as a function of temperature.

that the regular crystals, which look like whiskers, were formed in a gas-phase reaction. Possibly, the hydrogen contained in the atmosphere allowed an intermediate formation of AlH_3, which decomposed again and formed AlN.

During calcining, the formation of radicals was observed by electron spin resonance (ESR)-spectroscopy. The X-band spectra were recorded directly at temperatures up to 540 °C with the aid of a Bruker Spectraspin ER 414 equipped with a high-temperature resonator (ER 4114 HT). A very sharp signal at $g = 1.99$ without hyperfine splitting can be seen. Fig. 9 shows the intensity of that signal (peak-to-peak) in arbitrary units as a function of the temperature. In the cooled sample, an ESR spectra was recorded again and showed a relative peak intensity of 2.4. Samples with a constant spin density which is independent of temperature, generally show decreasing ESR signals at higher temperatures, due to decreasing overpopulation of the lower spin energy level. By contrast, in the sample investigated, an increase in intensity of the ESR signal at $g = 1.99$, was observed. This increase occurred in two steps, predominantly in the temperature ranges from 100–200 °C and from 300–450 °C; but it should be remarked that the spin density itself increases over the whole temperature range. It can be concluded that an extensive formation of radicals occurred during calcining, and that radical reactions play an important part during the pyrolysis process. Depending on the calcination atmosphere, the colour of the powder obtained was either nearly white (ammonia) or grey (nitrogen or nitrogen/hydrogen). Calcining in argon resulted in a black-coloured sample. The calcining process should be considered not only as a simple pyrolytic process but also as a chemical reaction with the calcination gas.

In order to study the calcination reactions, the precursor has been dried by simply attaching a vacuum pump to the vessel, and subsequently heating it. This procedure led to a relatively coarse powder, with a fairly broad particle size distribution. To obtain smaller particles and a more narrow particle size distribution, the precursor has to be dried by other methods. In this paper, this was achieved by dropping a precursor solution into a well-stirred paraffin, which had previously been heated up to a temperature of about 450 °C. Afterwards, the polymeric powder was obtained by filtration from the liquid paraffin. Although rinsed with petroleum ether, a small amount of paraffin remained, and the surface of the particles is presumed to be covered by a thin paraffin layer. Best results were obtained if the viscosity of the precursor solution was adjusted to a value of about 0.7 Pa s (at 20 s^{-1}) by adding propylamine. This procedure led to a drastic improvement of the powder fineness, and to a narrower particle size distribution. Fig. 10 shows scanning electron micrograph of a powder prepared by this method and calcined at 900 °C in an ammonia atmosphere. A very fine-grained powder can be seen; nearly all particles are in the submicrometre range.

During calcining, considerable quantitatives of organic compounds must be removed and vaporized. In order to obtain homogeneous and uniformly coloured products, the polymers have to be calcined using a relatively high rate of flow of the calcination gas. Thus, the gas flow should be distributed as homogeneously as possible around all particles. The best results were obtained if the powder was treated through carbon felt.

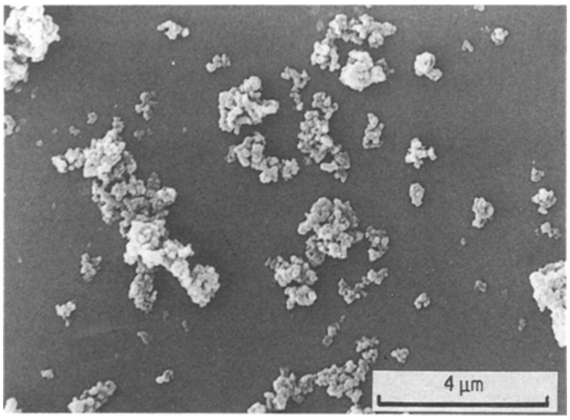


Figure 10 Scanning electron micrograph of a powder, dried in hot paraffin and calcined in ammonia at 900 °C.

Table I shows the oxygen content, measured by high-temperature extraction (Leco TC 136), and carbon content, of powders prepared by different drying and calcining procedures. Best results were obtained if the calcination was carried out in ammonia. Although the powder obtained by hot paraffin drying, possessed a much smaller mean grain size, the oxygen content was slightly lower. It may be assumed that this is due to the thin paraffin layer obtained, which is presumed to protect the polymeric powder from a reaction with moisture and oxygen. This would facilitate the handling of the powder before calcining. During calcining, residual paraffin is evaporated. After calcining, the sensitivity to moisture and air decreases drastically, but an increase of about 0.25 wt % atomic oxygen per day is still observed when spreading the powder in laboratory atmosphere.

4. Sintering

The calcined powders were isostatically cold pressed without any additives (480 MPa, 1 min). Powders calcined in nitrogen or argon atmospheres could not easily be pressed to green bodies without exfoliating. Powders calcined in ammonia could be densified to a green density of 56%–62% theoretical, depending on morphology. Therefore, sintering experiments were carried out only with powders calcined in ammonia. For sintering, a carbon-tube furnace purged with nitrogen was used, and the samples were embedded in aluminium nitride powder.

In a preliminary description [12], it has already been shown, that the dilatometric curve of samples produced from these polymeric-derived powders, without the use of any sintering aid, is shifted by about 180 °C to lower temperatures compared to conventionally produced powders (Tokuyama Grade F) using CaO as sintering aid.

At 1650 °C, the density of all samples was in the range of 92%–96% theoretical density, and the mean grain size was about 0.5 µm. At 1850 °C, fully dense samples with a mean grain size of about 5–7 µm were obtained. At temperatures of 1950 °C and more, the density decreased again, supposedly due to the evaporation of aluminium nitride. The density which could be achieved at temperatures below 1850 °C depended strongly on the powder processing. Powders of the type shown in Fig. 7 and prepared by simply evaporating organic compounds from the precursor solution, could not be completely densified at 1820 °C. By contrast, dense samples (> 99% theoretical density) could be prepared at this temperature from powders,

TABLE I Oxygen content of powders dried by different procedures and calcined in different atmospheres

Drying procedure[a]	Calcination gas	Oxygen content (wt %)	Carbon content (wt %)
Evaporating	NH_3	2.2	< 0.8
Evaporating	N_2	2.5	1.6
Evaporating	Ar	1.8	~ 20
Hot paraffin	NH_3	1.9	< 0.8

[a] See text.

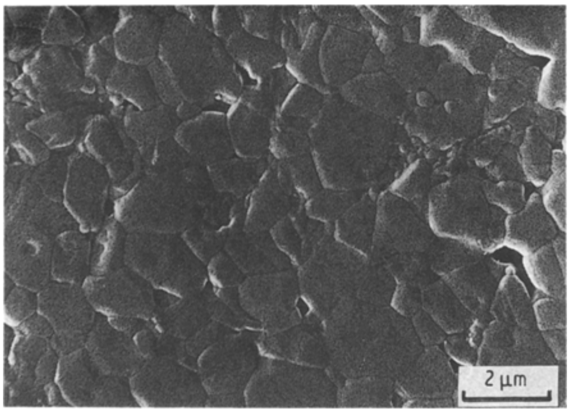


Figure 11 Scanning electron micrograph of a sample sintered at 1820 °C; powder prepared by evaporating organic compounds from the liquid precursor.

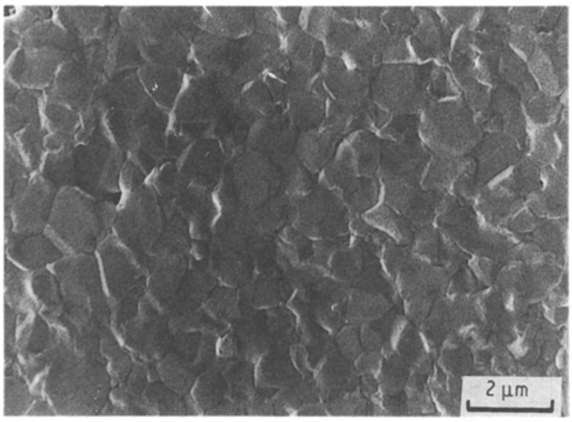


Figure 12 Scanning electron micrograph of a sample sintered at 1820 °C; powder prepared by hot-paraffin drying.

prepared by hot-paraffin drying. Fig. 11 shows a scanning electron micrograph of a sample prepared from a powder dried by simply evaporating the organic compounds; the mean grain size is about 2 μm and the porosity about 3%; some pores are still fairly large. Fig. 12 shows a scanning electron micrograph of a sample prepared from hot-paraffin dried powder. The microstructure is more homogeneous, the mean grain size seems to be slightly smaller, and only very few small pores can be seen.

5. Conclusions

Fluid aluminium nitride precursors, prepared by anodic dissolution of metallic aluminium in a fluid organic electrolyte, were dried by simply evaporating organic compounds, and by hot-paraffin drying. The calcination process is not only a simple pyrolytic process, with the formation of large amounts of radicals, but also a chemical reaction with the calcination gas. Therefore the interaction with the calcination atmosphere, and thus the chemical composition of calcined powders, depends strongly on powder morphology and the drying procedure of the polymeric precursor. Best results were obtained by hot-paraffin drying and calcination in ammonia on carbon felt. Sintering experiments proved that aluminium nitride powders prepared by this procedure could be densified at 1820 °C to samples with a density of > 99% theoretical density, while samples prepared from conventionally dried precursors had higher porosity and a less homogeneous microstructure.

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References

1. W. WERDECKER and F. ALDINGER, in "Proceedings of the 34th ECC", IEEE Transactions on Compounds, Hybrids and Manufacturing Technology, Vol. CHMT-7, No. 4 (IEEE 1984) p. 399.
2. Tokuyama Soda Co. Ltd, SHAPAL Technical Bulletin No. 8102 and SHAPAL-M Technical Bulletin No. 6102 (Tokuyama Soda Co. Ltd, Tokyo, Japan, 1987).
3. D. FISTER, *Ceram. Engng Sci. Proc.* **6** (1985) 1305.
4. M. BILLY and J. MEXMAIN, *Sprechsaal* **118** (1985) 245.
5. I. KIMURA, N. HOTTA, H. NUKUI, N. SAOITO and S. YASUKAWA, *J. Mater. Sci. Lett.* **7** (1988) 66.
6. G. POUSKOPULELI, *Ceram. Int.* **15** (1989) 213.
7. M. F. LAPPERT, "Metal and Metalloid Amides" (Wiley, New York, 1980) p. 99.
8. L. V. INTERRANTE, in Materials Research Society Symposium Proceedings, Vol. 32, edited by C. J. Brinker "Better Ceramics through Chemistry II", (Materials Research Society, Pittsbourgh, 1986) p. 359.
9. L. MAYA, *Adv. Ceram. Mater.* **1** (1986) 150.
10. S. CUCINELLA, *J. Organometall. Chem.* **8** (1967) 312.
11. M. SEIBOLD and C. RÜSSEL, *J. Amer. Ceram. Soc.* **72** (1989) 1503.
12. M. SEIBOLD and C. RÜSSEL, in Materials Research Society Symposium Proceedings, Vol. 121, "Better Ceramics Through Chemistry III", edited by C. J. Brinker, D. F. Clark and D. R. Ulrich, (Materials Research Society, Pittsbourgh, 1988) pp. 477–82.

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