

Alumina-Coating of Silicon Nitride Powder

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Abstract

α -Silicon nitride powder has been coated with aluminium oxide generated by the in-situ hydrolysis of aluminium isopropoxide in isopropanol solution. TEM examinations show clearly the coating structure and the homogeneity of dispersion of the aluminium oxide over the surfaces of the silicon nitride particles. Benefits of this method of addition of densification additives are shown in a faster sintering densification rate of coated particles compared with conventionally mixed powders, and in the homogeneity of the final microstructure.

α -Siliziumnitrid-Pulver wurde mit Aluminiumoxid beschichtet, welches durch in-situ Hydrolyse einer Lösung von Aluminium-Isopropoxid in Isopropanol hergestellt wurde. TEM-Untersuchungen zeigen sehr deutlich die Struktur der Beschichtung und die Gleichmäßigkeit der Verteilung des Aluminiumoxids auf den Oberflächen der Siliziumnitrid-Teilchen. Vorteile dieser Methode der Zugabe von Verdichtungsadditiven manifestieren sich in einer höheren Verdichtungsrate der beschichteten Teilchen beim Sintern im Vergleich zu konventionellen Pulvergemischen und in der Homogenität des Endgefüges.

De la poudre de nitrure de silicium α a été recouverte d'une couche d'oxide d'aluminium générée par hydrolyse in-situ d'isopropoxide d'aluminium dans une solution d'isopropanol. Les clichés de MET montrent clairement la structure de recouvrement, et la dispersion homogène de l'oxide d'aluminium sur les surfaces des particules de nitrure de silicium. Les avantages d'une telle méthode d'addition de liants sont une vitesse de frittage plus élevée des particules

recouvertes d'oxide d'aluminium comparé aux mélanges de poudres traditionnels, et une plus grande homogénéité de la microstructure finale.

1 Introduction

Many ceramic systems are sintered with the aid of liquid-forming additives and it is important for the final sintered microstructure that the sintering additive is blended with the major phase particles as homogeneously as possible. Good dispersion of the components of the active liquid also assists the rapid development of this liquid, the achievement of maximum extent of contact with the solute phase, and thus accelerated densification rates. This is especially useful for systems which are difficult to sinter to full density and for which particularly good dispersion of the sintering aid is required; silicon nitride is one of the materials in this category. For this reason the use of milled oxide or similar powders as a means of adding the sintering aid has been common. More recently, well-established methods for coating pigment particles with hydrated oxide or hydroxide films^{1,2} have been extended to the ceramics field, and it is recognised that the production of coated particles by a hydrolytic method is, in principle, preferable to the simple production of mixed powders by this technique. One added advantage of using coated particles is that the particle takes on the surface characteristics of the coating material, and may then show improved handling characteristics in the dried or dispersed state.

The development of coatings in ceramic systems, as opposed to the relatively uncontrolled bulk precipitation of the additive component, is now receiving increased attention, but it is far from clear

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Table 1. Sintering additive additions by precipitation in silicon nitride systems

<i>Additive element</i>	<i>Starting compound</i>	<i>Solvent</i>	<i>Precipitant</i>	<i>Reference</i>
Ce/Y	Isopropoxide	Benzene	Water	3
Al	Isopropoxide	Tetrahydrofuran	Water	4
Mg	Nitrate	Isopropanol	Water	5
Mg/Y	Nitrate	Water	Tetraethylammonium hydroxide	6
Al	Isopropoxide	<i>n</i> -Hexane	Water	7
Al/Ti	Isopropoxide	<i>n</i> -Hexane	Water	8
Al/Mg	Isopropoxide	Isobutanol	Water	9
Y/Al	Nitrate	Water	NH ₄ OH	10

that techniques for the production of coated ceramic particles have been optimised, or the behaviour of the coating phase and the coated particles fully characterised. Examples of the use of precipitation and co-precipitation reactions to blend sintering additive components to silicon nitride powders are listed in Table 1.

Evidence for the formation of coatings on the silicon nitride particles is in part direct (TEM observations on the surfaces of individual particles¹⁰) and in part indirect, making use of zeta-potential measurements which show a slow transformation of the zeta-potential as a function of pH curve from that characteristic of the uncoated silicon nitride to that of the coating material with increasing loading of coating phase. This second type of proof of the existence of a particle coating suffers from the weakness that mechanically milled powder mixtures (silicon nitride and calcined coating material) also show zeta-potential curves intermediate between those of the two separate components.⁹ However, the extent of the shift of the zeta-potential curve is far greater in the case of oxides precipitated in the presence of dispersed silicon nitride powder than those simply mechanically mixed, which could be taken to be indicative of a coated particle. The stage at which the coating develops is not established conclusively by either reported method, because both use previously dried powders and it cannot be ruled out that deposition of the coating material occurred from a suspension during the drying stage, and not during the precipitation stage.

The coating oxide powders examined have had, on the basis of specific surface area and XRD line-broadening measurements, primary particle dimensions of the order of 15–40 nm.⁹ Where coated particles have been examined at high magnification by TEM it has been clear that the term 'coating' is not always strictly accurate. The coating phase is of particulate morphology, possibly of low density, and adheres non-uniformly to the underlying substrate

particle. It is clear that much of the particle area may not be receptive to the coating phase, which therefore tends to develop into a mass of finely particulate material occupying the interparticle regions. Much of the coating phase may in one sense therefore be 'wasted', although it still represents the addition of a sintering aid in a very finely divided and relatively well-distributed form. On the other hand, for powders which are difficult to sinter, such as silicon nitride and silicon carbide, there is considerable advantage in having all the additive phase distributed as a well-bonded coat, maximising initial contact with the sintering particles.

In most previous work with silicon nitride powders no difficulties have been reported with the handling or compaction of coated powders in preparation for sintering. This may have been because the coating process was carried out in a non-aqueous solvent with restricted amounts of water. It has been noted that oxide powders dried from non-aqueous media, in which hydrogen bonding forces are weaker, show a lesser tendency to form hard agglomerates.¹¹ When water was used as the solvent during precipitation of a coating phase from a nitrate solution the formation of hard agglomerates was reported to create a significant problem, and as a result of subsequent differential sintering of the agglomerates densification behaviour was poor unless further extensive milling to break down the agglomerates was carried out.¹⁰

It is clear that sintering additive particle size and homogeneity of dispersion within the silicon nitride are both factors favouring the densification of the silicon nitride. Sintering of coated powders has been reported to be faster,⁹ and even when no special precautions have been taken to ensure development of a coherent coating, higher sintered densities and strengths may be obtained under set conditions using in-situ precipitation of the sintering additive, by comparison with those obtained from mechanically mixed powders.¹²

The work reported here was carried out in order to gain more information about the nature, qualities and behaviour of the coating, and to try to quantify the benefits of using coated particles for the development of sintered materials. A simple model system of aluminium oxide–silicon nitride was selected for the first stage of this study. This system leads to the formation of β '-sialon as the major phase, but aluminium oxide is a common component of many silicon nitride sintering additive systems, and a detailed study of its behaviour is seen as providing the starting point for development to more complex systems. Hot-pressing was used as a rapid means to achieve densification for initial assessment of microstructural homogeneity.

2 Experimental

The silicon nitride powder used (H. C. Starck, LC12-N, Germany) was 96% α -phase, which had a specific surface area (a_s) of $17.4 \text{ m}^2 \text{ g}^{-1}$ and a mean particle size of 500 nm as determined by a standard sedimentation measurement (Micromeritics, 'Sedigraph' 5000ET, USA). Aluminium isopropoxide (BDH, Poole, UK) was dissolved in dry isopropanol (BDH, Poole, UK) to give a concentration of $5 \text{ g}/100 \text{ cm}^3$. Silicon nitride powder was added to the solution and dispersed by ball-milling for 24 h in a polyethene bottle with cylindrical silicon nitride grinding media of total mass three times that of the powder. After mixing the slurry was transferred to a beaker and heated to 75°C with vigorous magnetic stirring while a 33 vol.% solution of isopropanol was added dropwise at an overall rate of $3 \text{ cm}^3 \text{ min}^{-1}$. To ensure complete hydrolysis of the aluminium isopropoxide a water/isopropoxide molar ratio of 20:1 was used, based on the work of Bostedt *et al.*¹³ The slurry was slowly stirred at 22°C for a further 24 h and then dried on a hot-plate.

Batches of silicon nitride powder were coated with aluminium hydroxide to give the equivalents of 5, 15 and 25 weight% of aluminium oxide. Pure coating material (aluminium oxide) was also prepared for comparison purposes by the same route.

Coated powders were examined using several techniques. Simultaneous differential thermal and thermogravimetric analysis (STA 780, Stanton, UK) was carried out at a heating rate of 5°C min^{-1} in flowing air. Zeta-potentials of powders suspended in water were measured at a range of pH values ('Zetasizer II', Malvern, Cambridge, UK). The mobility measurements were carried out using suspensions of 0.2 mg cm^{-3} in 1 mol m^{-3} KCl solution as electrolyte buffer. pH was adjusted using dilute hydrochloric

acid or aqueous ammonia. Before measurements were taken the suspensions were ultrasonically vibrated and magnetically stirred to disperse agglomerates. At least four measurements were made at each pH value.

The nature of the coating layers was observed directly using TEM. Dilute dispersions of powder in isopropanol were prepared by ultrasonically vibrating for 10 min, and a drop of suspension was evaporated on a Formva-covered and carbon-coated copper grid. Phase compositions in coating materials were determined by XRD (CuK_α radiation with a scanning speed of $0.05^\circ \text{ s}^{-1}$).

Further examinations of coated powders were made after centrifuging to endeavour to separate the larger coated silicon nitride particles from any finer, detached, aluminium oxide or hydroxide particles remaining in the suspension. This was done with progressive increase in centrifuge speed, intended to give a striated centrifuged deposit, the sections of which would correspond to increasingly finer particle size fractions. The suspension of silicon nitride was diluted immediately after completion of hydrolysis of the aluminium isopropoxide to a concentration of 20 mg cm^{-3} and vibrated ultrasonically for 5 min. Centrifuging (Europa, 24M, Germany) was carried out at speeds between 10 and 140 Hz. The sedimented cake was carefully removed from the centrifuge tube, dried and isostatically pressed at 300 MPa to give sufficient strength to allow cutting into thin discs representative of the bottom, middle and top layers. Samples of these layers were set in epoxy resin, polished and analysed with respect to the Al/Si ratio microanalysis (XMA) under the scanning electron microscope.

In order to quantify powder compaction behaviour, 300 mg of each powder was pressed without additions in an 8.5 mm diameter die using standard testing equipment (Instron, Universal type 1153, UK) over the pressure range 3 to 210 MPa. This quantity of powder gave pellets of thickness to diameter ratio of 0.4, minimising frictional effects between the powder and the die.¹⁴ Corrections were made for die elasticity and systematic machine errors, on the basis of the compression behaviour of the empty die. Relationships between compact density and applied pressure were obtained from the final pellet thickness and density, and the preceding cross-head movement.

Specific surface area values were measured using a single-point nitrogen adsorption method (Perkin-Elmer 212D Sorptometer, USA) and the standard BET equation. Each quoted value is the average of three determinations.

To compare the densification behaviour of coated powder with that of powder prepared by ball-milling, samples with the same composition (15 weight% aluminium oxide) were hot-pressed at 1750°C under 15 MPa for 10 min in a graphite die, the internal surfaces of which had been coated with a wash of boron nitride powder. Sintering shrinkage was monitored continuously using a linear displacement transducer; data were stored on disc for subsequent processing to give density as a function of time and instantaneous densification rate as a function of time. The only difference between the two powders was the method of incorporating the densification aid. The ball-milled mixture was prepared by milling the silicon nitride with aluminium oxide powder (Realox-XA-1000SG, Alcoa, USA, with a median particle size of 500 nm) in isopropanol for 24 h followed by rotary evaporation drying. Both types of silicon nitride powder mixture were calcined in air at 800°C for 2 h before pressing. Densities of dense hot-pressed materials were obtained by mensuration, and polished surfaces were examined by light microscopy (LM), and by scanning electron microscopy (SEM) after etching with molten KOH at 500°C for 60 s.

3 Results

Figure 1 shows the uncoated silicon nitride powder. The nature of the pure hydrated alumina coating materials as obtained by precipitation from isopropanol solutions at 75°C, and after drying at 120°C, is shown in Fig. 2. After calcination at 800°C some crystallisation of this phase occurs (Fig. 3). The inset electron diffraction patterns show the poorly crystalline nature of the as-precipitated material,

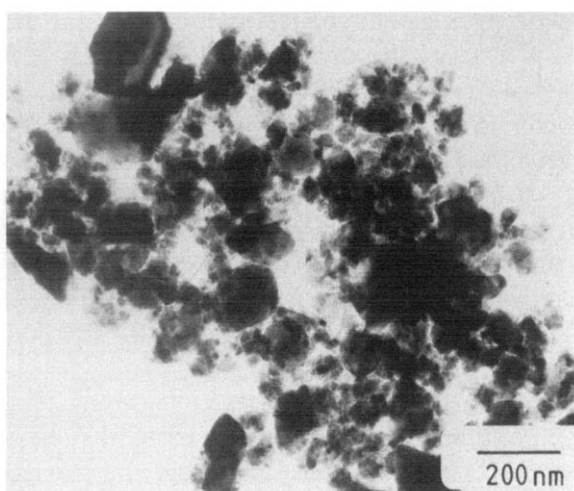


Fig. 1. Transmission electron micrograph of uncoated Si_3N_4 powder.

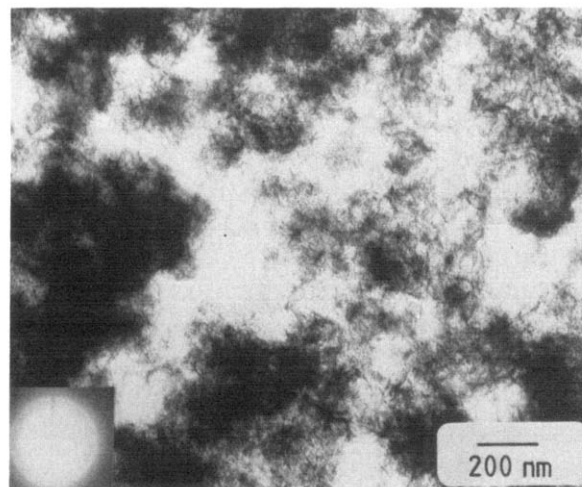


Fig. 2. Transmission electron micrograph of as-precipitated bulk hydrated aluminium oxide.

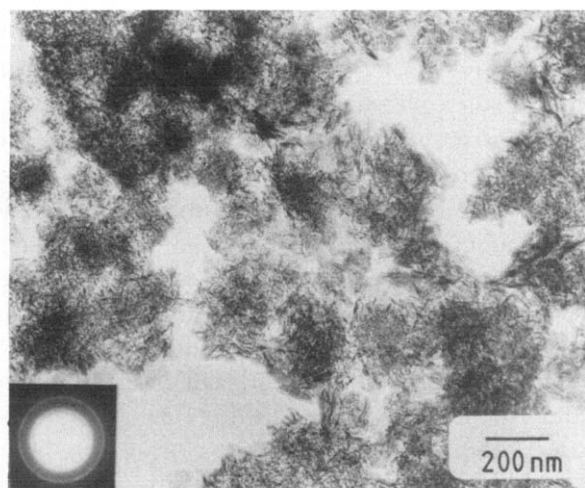


Fig. 3. Transmission electron micrograph of pure coating phase after calcination at 800°C for 1 h.

and the formation of a very fine particle size material after calcination, consistent with the TEM images. These forms are also those of the as-precipitated and calcined coatings on the silicon nitride particles, as shown in Figs 4 to 8; after calcination at 800°C the structure is more clearly crystalline. The thermal behaviour of the pure coating material, and that of a 25% coated silicon nitride powder, is indicated in terms of mass loss and differential thermal analysis (DTA) curves in Fig. 9. The sharp peaks at 1000°C would be expected to be those of a δ - to θ - Al_2O_3 transition.¹⁵ a_s data for dried silicon nitride powders coated with 5, 15 and 25 weight% of hydrated alumina are shown in Fig. 10. The effect of calcination on the specific surface area of a 25% coated silicon nitride powder is shown in Fig. 11.

XRD examination of the pure coating material after drying at 120°C shows (Fig. 12) a high, broad background, probably attributable to amorphous or

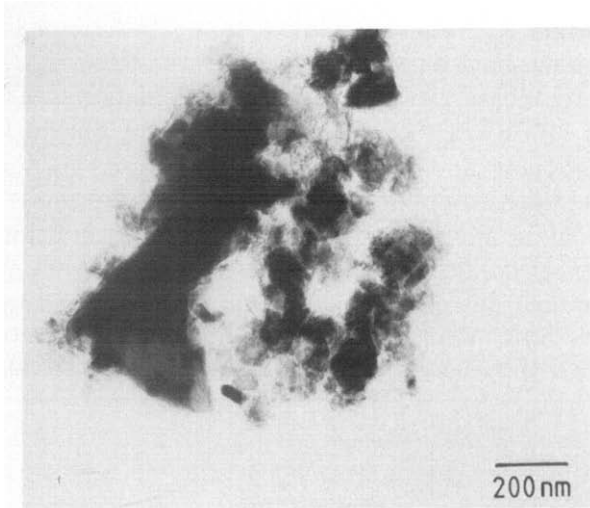


Fig. 4. Transmission electron micrograph of silicon nitride particles coated with 5 wt% hydrated alumina.

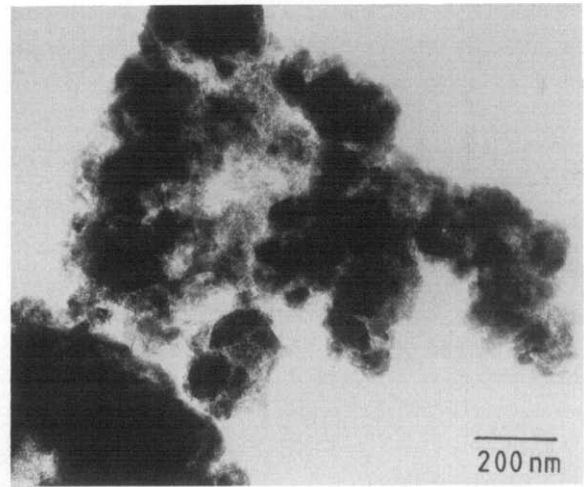


Fig. 7. Transmission electron micrograph of silicon nitride particles with 25 wt% coating after calcination at 300°C for 1 h.

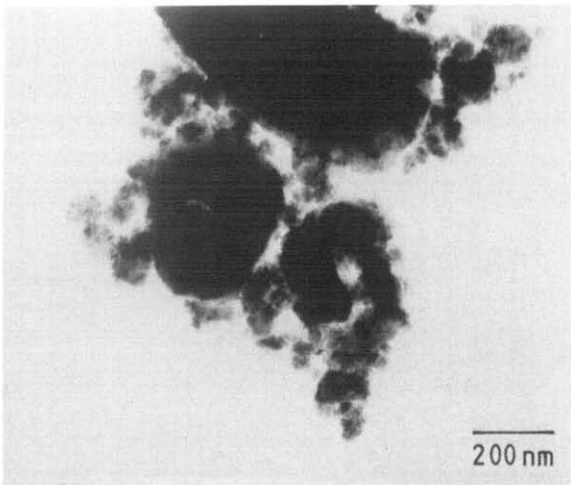


Fig. 5. Transmission electron micrograph of silicon nitride particles with 5 wt% coating after calcination at 800°C.

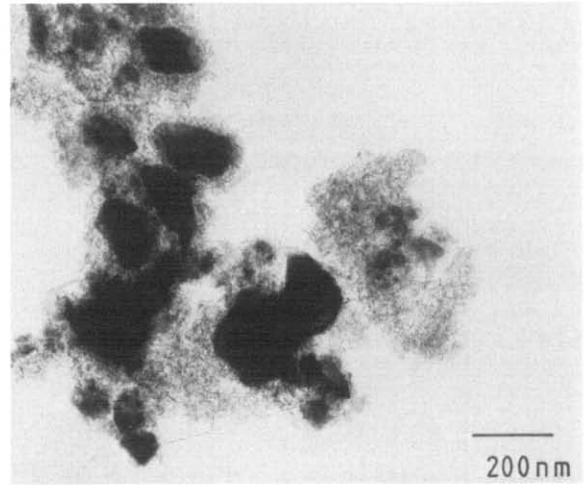


Fig. 8. Transmission electron micrograph of silicon nitride particles with 25 wt% coating after calcination at 800°C for 1 h.

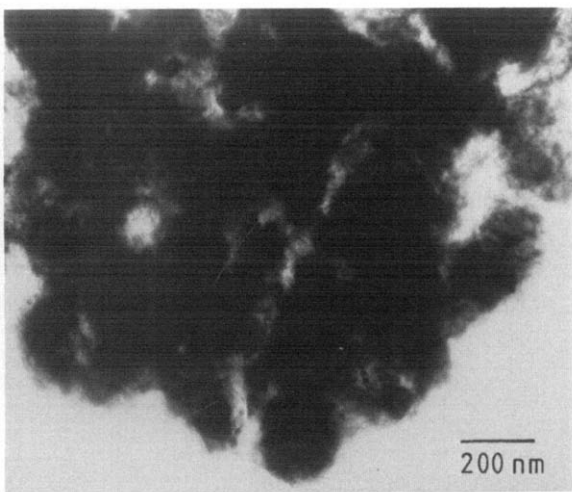


Fig. 6. Transmission electron micrograph of silicon nitride particles coated with 25 wt% hydrated alumina.

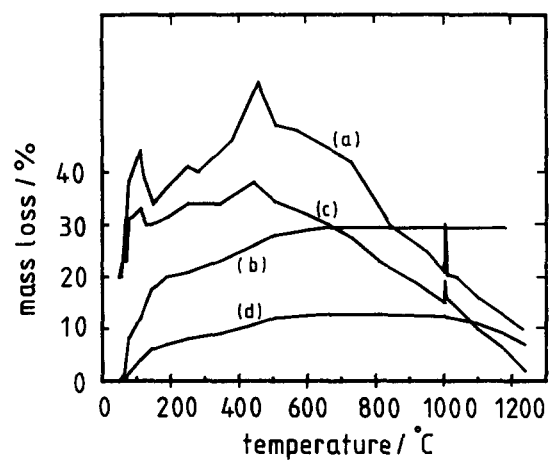


Fig. 9. DTA ((a) and (c)) and TGA ((b) and (d)) curves for pure coating ((a) and (b)), and 25 wt% coated powder ((c) and (d)). The DTA peaks represent exothermic processes.

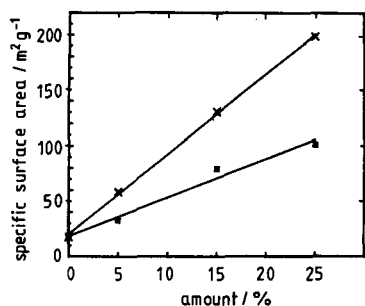


Fig. 10. Coated silicon nitride specific surface area as a function of coating amount. x, Dried; ■, calcined.

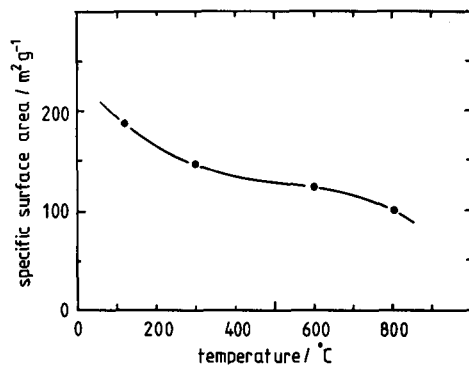


Fig. 11. Coated silicon nitride (25 wt% coating) specific surface area as a function of calcining temperature.

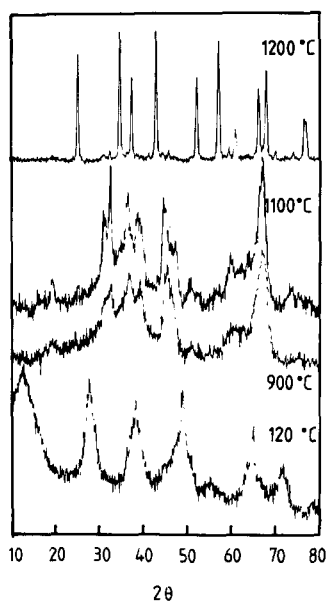


Fig. 12. XRD traces of precipitated hydrated aluminium oxide dried at 120°C, and after calcination for 2 h at 900, 1100 and 1200°C.

very poorly crystalline material, and broadened peaks indexed as those of 'boehmite' (γ -AlO₃·OH).¹⁶ Calcination of this material for 2 h at 900°C leads to the loss of the boehmite peaks, and their replacement by peaks assumed to be those of σ -alumina. There is little further change during 2 h calcination at 1100°C, but after 2 h at 1200°C complete conversion to α -alumina has taken place. Ervin¹⁷ and other

workers¹⁸⁻²⁰ have claimed that all 'transient' aluminas have a peak at or near 199 pm ($2\theta = 45.8^\circ$). This is a feature of the products of calcination at 900 and 1100°C of the precipitated alumina, but peak broadening and background noise caused by the high signal amplification needed with the poorly crystalline material make more precise identification of phase difficult. It has been reported¹⁵ that γ -alumina transforms to δ - and θ -aluminas on heating to >850°C, and finally to α -alumina at 1150°C. In the present case no α -alumina peaks were detectable

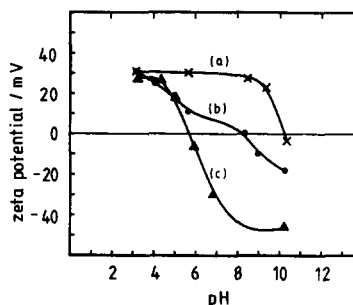


Fig. 13. Zeta-potential as a function of pH for (a) coating phase, (b) coated silicon nitride (25 wt%) and (c) silicon nitride.

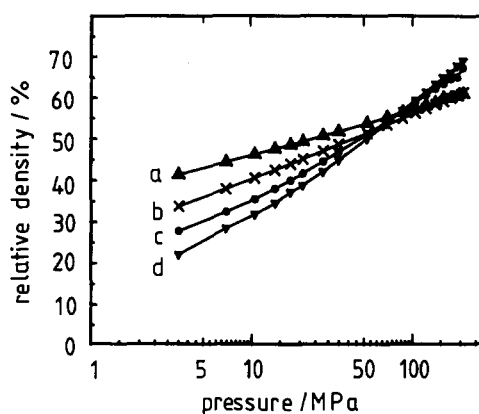


Fig. 14. Relative density as a function of compaction pressure for as-coated powder of different coating amounts. (a) 0%; (b) 5%; (c) 15%; (d) 25%.

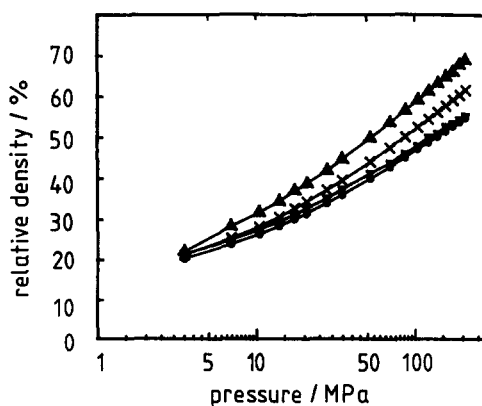


Fig. 15. Relative density as a function of compaction pressure for 25 wt% coated powder after calcination for 1 h at different temperatures. ▲, 120°C; x, 300°C; ▼, 600°C; ●, 800°C.

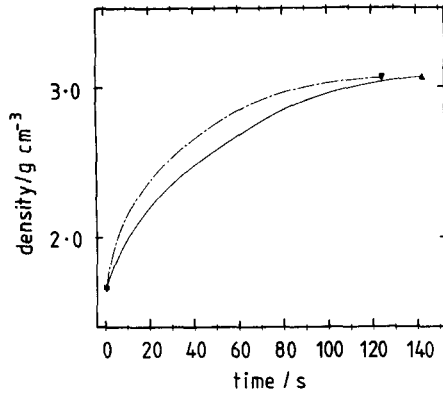


Fig. 16. Density as a function of time during hot-pressing at 1750°C and 15 MPa. ▲, Mixed; ▼, coated.

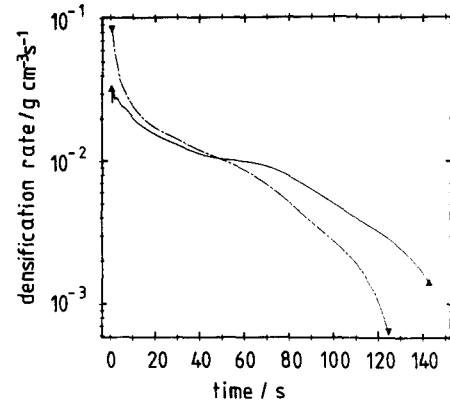


Fig. 17. Densification rate as a function of time; data derived from Fig. 16. ▲, Mixed; ▼, coated.

after calcination for 2 h at 1100°C, in spite of the sharp DTA peak seen at 1000°C.

The EDS analyses of the bottom, centre and top layers of the centrifuged silicon nitride cake showed a constant (within experimental error) Al/Si peak height ratio of 0.12, and irrespective of the position in the cake from which the sample was taken. This is in agreement with the calculated atomic ratio in the mixture. Zeta-potential measurements made on powders with varying amounts of coating phase are shown in Fig. 13. It is seen that the curve of the 25%

coated material is intermediate between those of uncoated silicon nitride and the pure coating phase, with an isoelectric point at pH 8. Continuous compaction characteristics of the uncoated and coated powders were analysed in terms of bulk density as a function of compaction pressure. Densification curves are shown in Fig. 14 for the dried as-prepared coatings, and after calcination before compaction, in Fig. 15. Powder densities before and after calcination were determined by a standard Archimedes method.

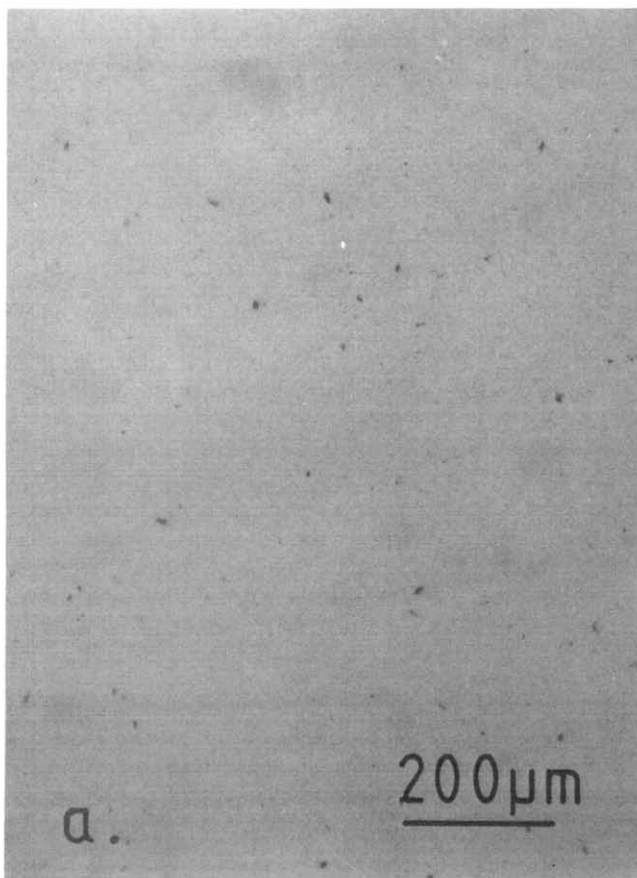


Fig. 18. Microstructures of hot-pressed materials: light micrographs of polished surfaces of materials prepared from (a) coated powder and (b) mechanically mixed powder.

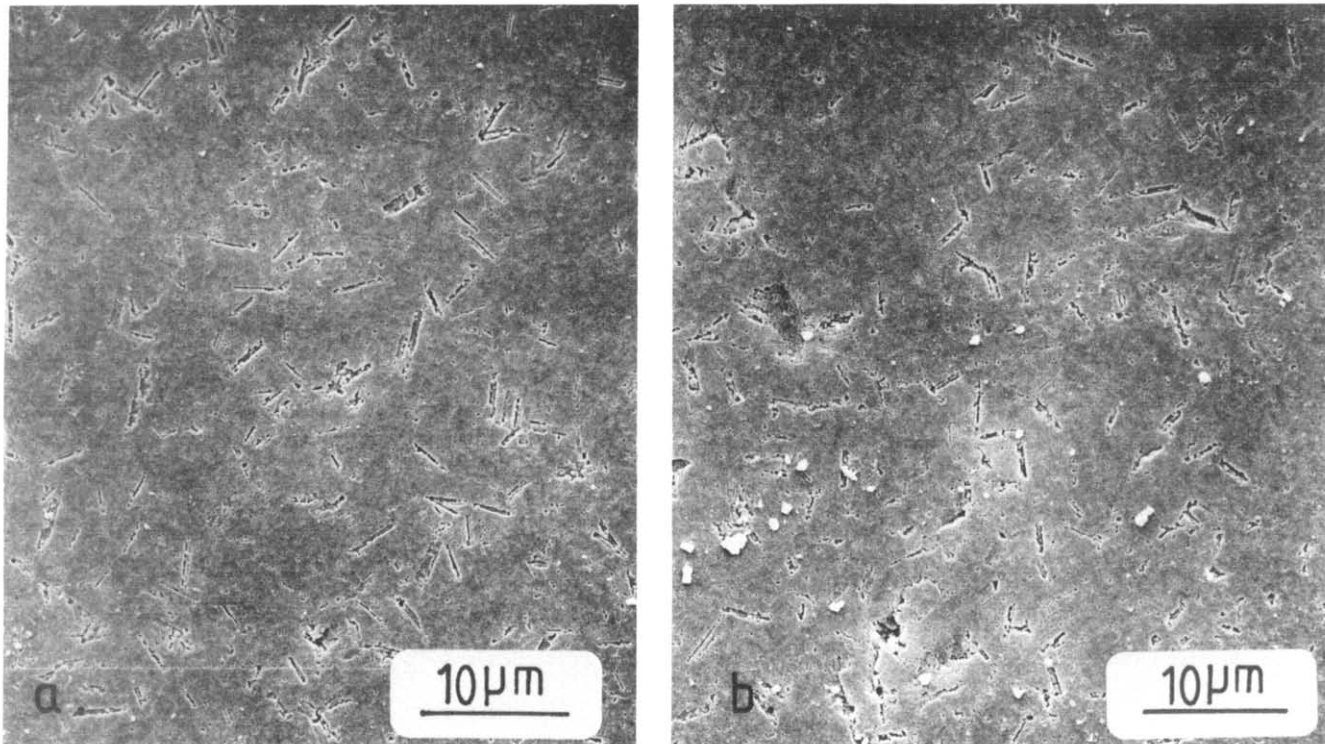


Fig. 19. SEM photographs of polished and KOH etched surfaces of materials prepared from (a) coated powder and (b) mechanically mixed powder.

Densification behaviour during hot-pressing at 1750°C under 15 MPa of uncoated mixed powder, and of silicon nitride powder coated with 15 weight% aluminium oxide, is shown in terms of density as a function of time in Fig. 16, and of densification rate as a function of time in Fig. 17. LM micrographs of polished surfaces of fully dense chemically coated and mechanically mixed materials are shown in Fig. 18. Figure 19 shows a similar pair of SEM micrographs of polished and etched surfaces.

4 Discussion

This examination of an alumina-coated nitride powder has shown the nature of the coating phase, and its behaviour during the subsequent steps of a ceramic fabrication route. The hydrated alumina coating is in reality a thin, low-density layer of amorphous or finely particulate crystalline material which adheres fairly strongly to the silicon nitride particle surfaces. The coating has a very high specific surface area, and an open structure which should not prevent access of other species of ionic dimension to the underlying silicon nitride surface. It seems likely, from observations made on selectively centrifuged coated powders, that the adhesion of the hydrated alumina to the silicon nitride particles occurs during

the precipitation stage, and not subsequently during the drying stage. If coating only took place on drying, a variation in the Al/Si ratio in the centrifuged powder would be expected between the lower (expected to be Si-rich) and upper (Al-rich) layers of the cake. There is thus in this sense a real 'coating' of nm particles which might be assumed to nucleate and grow on silicon nitride surfaces, rather than a 'deposit' formed around the silicon nitride particles during the concentration of a colloidal suspension of hydrated alumina and which is therefore simply a 'mixture' of particles. With small amounts of coating (<10%), the alumina is concentrated almost entirely at the silicon nitride particle surfaces. Larger amounts lead to the development of 'clumps' of agglomerated coating particles which may bridge and bind several silicon nitride particles. From the point of view of the homogeneity of distribution of the coating phase, this state is clearly undesirable, and there thus appears to be a practical limit to the amount of additive which can be incorporated into a powder as a strict 'coating'. With the 100 nm or so silicon nitride particles used here this limit appears to be at around the 10 weight% level.

Even though the underlying silicon nitride surface would be expected to be accessible to ionic species, the overall electrical nature of the particle is dominated by adsorbed species at the much higher

specific surface area of the 2 nm dimension particles forming the coating (estimated on the basis of the BET measurements giving an a_s value of $200 \text{ m}^2 \text{ g}^{-1}$ for 25 vol. % coating); the surface electrical potential of the particles is predominantly, though not entirely, that of the coating material. It is of interest in this context that the zeta-potential characteristics of the coating material are those of a hydrated γ -alumina with an isoelectric point in the region of pH 10, and not those of α -aluminium oxide, which would be expected to have an isoelectric point in the region of pH 7. The specific surface area of the coating falls by 50% after annealing at 800°C for 2 h, consistent with the morphological changes seen by TEM (Figs 6 and 8).

The low density nature of the coating particles is also demonstrated clearly by the compaction behaviour of the coated silicon nitride powder. This shows two marked features. The first is the low packing density obtained with low ($<10 \text{ MPa}$) compaction pressure. The second is that the compressibility of the coating is very high, and at pressures $>100 \text{ MPa}$ significantly higher packing densities can be achieved as the soft coating plastically deforms to occupy much of the silicon nitride particle inter-void space. Densities in the region of 70–80% can readily be obtained with uncalcined 15–25% coated particles with isostatic pressures of 200–300 MPa. This effect is shown schematically in Fig. 20 and the actual effect of compaction on the nature of the coating itself is shown in Fig. 21, for which the compacted powder was lightly ground and dispersed in isopropanol for collection of smaller fragments on a TEM grid. The practical consequence of this type of compaction behaviour is that to obtain full benefit from the coated particles, powder compaction pressures must be higher than those used for an uncoated powder. However, the high green densities obtainable carry obvious additional advantages in shortening the time required to achieve full sintered density. On calcination the more crystalline coating material becomes less plastic, and such high densities cannot

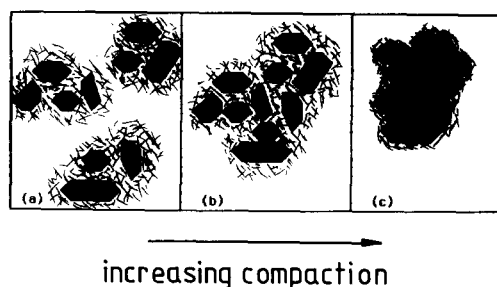


Fig. 20. A schematic representation of microstructural changes taking place during compaction.

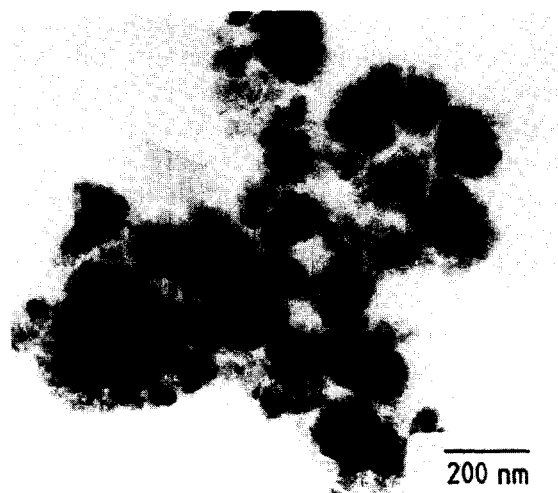


Fig. 21. Transmission electron micrograph of silicon nitride powder coated with 25 wt% hydrated aluminium oxide after compaction at 300 MPa.

now be so readily attained. Thus, if calcination is seen as a necessary stage prior to sintering, it should be carried out after compaction of the green body, and not before.

The advantages at the sintering stage of using coated silicon nitride powder are confirmed by the continuously recorded and computer-processed densification curves of Figs 16 and 17. The coated powder reaches the final recorded density of 3.06 g cm^{-3} significantly faster than the milled mixed powder. The initial stage (to 20 s) densification rate of the coated powder is faster by a factor of 2–3. This is in spite of the relatively low compaction pressure (20 MPa) applied cold to the powder in the graphite die, and thus the much lower cold green density of the coated powder compared with that of the conventionally milled powder. The faster initial densification rate seems likely to be the result of a more rapid generation of liquid phase on attainment of densification temperature. The milled powder shows a slight densification rate plateau at 60–80 s, attributable to an increase in the volume of liquid present in the system at this stage, the expected result of a slower reaction involving a relatively coarse (500 nm) aluminium oxide powder. Behaviour similar in principle is seen in the case of silicon nitride powder densified with a magnesium oxide–iron mixture, and attributed in this case to the slow formation of iron silicide.²¹

Microstructural examination of polished dense materials, and of polished materials after KOH etching, showed small but significant differences between materials prepared from coated powders and those prepared from mechanically mixed powders, and which could be attributed to improved homogeneity of additive mixing in the case of the

coated powders. The light micrographs of Fig. 18 show that although neither material is fully dense, the mean void size of material obtained by hot-pressing thin-coated powder is smaller than that of material prepared from mechanically mixed powder. The existence of large voids in the latter suggests local 'dry' regions, deficient in liquid-producing aluminium oxide. Both microstructures are generally uniform, but KOH etching (Fig. 19) reveals the existence of regions richer in intergranular silicate in the case of material prepared from mixed powders. The number of large, high aspect ratio silicon nitride grains detached during etching is larger in the case of material obtained from mechanically mixed powder, suggesting that there is inhomogeneity in the distribution of a glass-rich intergranular phase which, once removed by etching, allows surface silicon nitride grains to be released.

Overall the differences between the microstructures shown by these methods of examination, although clear, are not as marked as might have been expected, given the difference in starting particle sizes of the aluminium oxide additives. This suggests either that mechanical mixing of the fine 500 nm alumina and silicon nitride powders was quite effective, or that some microstructural coarsening occurs in the chemically precipitated aluminium oxide during heating to hot-pressing temperature. This type of grain-coarsening effect has been observed to blur in practice the distinction between a fine conventional, calcined and milled barium titanate powder, and one produced by a chemical coprecipitation route.^{22,23} Correspondingly greater differences in microstructure would have been expected if a coarser aluminium oxide powder had been used.

5 Conclusions

The formation of hydrated alumina by hydrolysis of aluminium isopropoxide in isopropanol solution in the presence of suspended silicon nitride powder leads to the development of coatings of nm dimensions of amorphous or partially crystalline particles, which can be fully crystallised by subsequent heat treatment. Coated silicon nitride powder shows poor compaction behaviour at low compaction pressures, but at pressures >200 MPa very high green densities can be obtained. The advantages of using the coating as a means of distributing a liquid-phase sintering additive are shown clearly by faster initial densification rates and overall improved microstructural homogeneity in

materials obtained from the coated powders, compared with conventionally ball-milled powders.

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References

1. Parfitt, G. D. (ed.), *Dispersion of Powders in Liquids*, 3rd edn. Applied Science, London, 1981.
2. Day, R. E. & Egerton, T. A., Surface studies of TiO₂ pigments with especial reference to the role of coatings. *Colloids and Surfaces*, **23** (1987) 137–55.
3. Mah, T., Mazdiyasi, K. S. & Rah, R., Characterization and properties of hot-pressed Si₃N₄ with alkoxy derived CeO₂ or Y₂O₃ as sintering aids. *Bull. Am. Ceram. Soc.*, **58** (1979) 840–4.
4. Kishi, K., Umebayashi, S., Tani, E. & Kobayashi, K., Synthesis of β -sialon from Si₃N₄ and aluminium isopropoxide. *Yogyo Kyokai Shi*, **93** (1985) 629–35.
5. Baik, S. & Raj, R., Effect of silicon activity on liquid phase sintering of nitrogen ceramics. *J. Am. Ceram. Soc.*, **68** (1985) C-124–C-126.
6. Shaw, T. M. & Pethica, B. A., Preparation and sintering of homogeneous silicon nitride green compacts. *J. Am. Ceram. Soc.*, **69** (1986) 88–93.
7. Kishi, K., Umebayashi, S., Pompe, R. & Persson, M., Interaction of alumino-iso-propoxide solution and Si₃N₄ powder. *J. Ceram. Japan. Inter. Edn*, **96** (1988) 687–9.
8. Kishi, K. & Umebayashi, S., Some mechanical properties of hot-pressed β '-sialon-TiN sintered body fabricated from α -Si₃N₄, aluminium-iso-propoxide and titanium-iso-propoxide. *J. Ceram. Soc. Japan*, **96** (1988) 725–30.
9. Kulig, M., Oroschin, W. & Greil, P., Sol-gel coating of silicon nitride with Mg–Al oxide sintering aid. *J. Eur. Ceram. Soc.*, **5** (1989) 209–17.
10. Kim, J. S., Schubert, H. & Petzow, G., Sintering of Si₃N₄ with Y₂O₃ and Al₂O₃ added by coprecipitation. *J. Eur. Ceram. Soc.*, **5** (1989) 311–19.
11. Xue, L. A., Riley, F. L. & Brook, R. J., *tert*-Butyl alcohol—a medium for freeze-drying: application to barium titanate. *Brit. Ceram. Trans. J.*, **85** (1986) 47–8.
12. Siegel, S., Herrmann, M., Klemm, H. & Kessler, S., High performance silicon nitride ceramics by homogeneous distribution of low content sintering additives. In *European Ceram. Soc., Second Conference*, Augsburg, 11–14 September 1991.
13. Bostedt, E., Persson, M. & Carlsson, R., Colloidal processing through surface modification. *Sci. Ceram.*, to be published.
14. Niesz, B. E., Bennett, R. B. & Snyder, M. J., Strength characterization of powder aggregates. *Bull. Am. Ceram. Soc.*, **51** (1972) 677–80.
15. Anon., *Aluminium Hydroxides and Oxides*. Alcoa Inc. Publication, 1989.
16. Mamoru, M. & Yuhji, Y., Preparation of Si₃N₄ and AlN powders from alkoxide-derived oxides by carbothermal reduction and nitridation. *Adv. Ceram. Mater.*, **2** (1987) 253–6.

17. Ervin, G. Jr, Structural interpretation of diaspor-corundum and boehmite- γ - Al_2O_3 transitions. *Acta Cryst.*, **5** (1952) 103-5.
18. Tertain, R., Papee, D. & Charrier, J., X-Ray studies of transition of anhydrides of alumina. *Compt. Rend.*, **238** (1954) 98-9.
19. Rooksby, H. P., Preparation of crystalline delta-alumina. *J. Appl. Chem. (London)*, **8** (1958) 44-9.
20. Rooksby, H. P. & Rooymans, C. J. M., Formation and structure of delta-alumina. *Clay Miner. Bull.*, **4**(1961) 234-8.
21. Stalios, A. D., Luyten, J., Hemsley, C. D., Riley, F. L. & Fordham, R. J., The interaction of iron during the hot-pressing of silicon nitride. *J. Eur. Ceram. Soc.*, **7** (1991) 75-81.
22. Alcock, J. R., Riley, F. L., D'Angeli, C. & Thomas, A. G., An evaluation of two barium titanate powder processing routes. *Brit. Ceram. Trans. J.*, **90** (1991) 152-6.
23. Wang, C. M., Riley, F. L., D'Angeli, C. & Thomas, A. G., Microstructural changes in chemically co-precipitated BaTiO_3 powder during heating. To be published.