JOURNAL OF MATERIALS SCIENCE 28 (1993) 3132–3136

Carbothermal synthesis of aluminium nitride at elevated nitrogen pressures

Part II *Effect of process parameters on particle size and morphology*

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The particle size and morphology of AlN product powders from carbothermal synthesis have been studied by scanning electron microscopy, surface-area measurement and microarea elemental analysis. AlN powders with widely variable grain size and morphology could be produced by varying the pressure, gas-flow rate and alumina type. Discrete AlN particles ($\sim$ 0.5–3 μm) were obtained by using fine γ-Al_2O_3 as starting material at 1600 °C over the pressure and gas-flow rate ranges 0.1–5 MPa and 1–10 l min^{-1}. When coarse α-Al_2O_3 was used as raw material, large aggregates of AlN particles normally formed, unless the reaction was run at high nitrogen pressure (5 MPa) and low gas-flow rate (1 l min^{-1}). Occasionally, whiskers formed at relatively low temperatures and pressures, e. g. 1500 °C and < 0.5 MPa. It was possible to obtain a discrete and fine AlN powder ($\sim$ 0.5 μm) without seeding. The results suggest that reactions including aluminium-containing gas species play an important role in the control of morphology in carbothermal synthesis of AlN.

1. Introduction

The excellent thermal conductivity and the high electrical resistivity of AlN make this material suitable for electronic ceramics, e.g. substrates for integrated circuits. In addition, the mechanical strength and thermal shock resistance are relatively high, and thus AlN may also find use as structural material [1].

For all applications, a method by which a suitable starting material can be produced at a low cost is desirable. The material should be a fine powder of high sinterability and purity. We are studying the carborthermal reduction and simultaneous nitridation of Al_2O_3 at elevated nitrogen pressures as a synthesis method for high-quality AlN powder. The nitrogen pressure was found to influence the conversion rate to AlN and the final carbon and oxygen impurity levels in the powder, as described in Part I of this work [2]. It was also found that quite different products, with respect to particle size and shape, could be produced by varying the process parameters pressure, gas-flow rate and alumina reactant type. This is accounted for in the present paper.

For the densification and sintering properties of a powder, the particle morphology, including the shape, size and size distribution is important. Achieving control of these powder characteristics is one objective for elucidating the reaction steps leading to AlN formation. Some attempts to this end will be described in this paper, based on a number of carbothermal nitridation runs at elevated nitrogen pressures.

2. Experimental procedure

The starting materials were five granulated mixtures, denoted A, B, C, D, and E, of alumina and carbon black powders, in three different mixing ratios (Table I). The α-Al_2O_3 powder (Fisher Scientific Co, "A-591") was relatively coarse (BET surface area $= 0.55\ m^2\,g^{-1}$) with a wide particle-size distribution, while the γ-Al_2O_3, made in-house by decomposition of ammonium alum, was fine-grained (< 1 μm, BET surface area $= 138\ m^2\,g^{-1}$) and poorly crystallized. Two carbon black powders (Nordisk Philblack Co.) were used; C, with mean diameter about 30 nm, BET area $82\ m^2\,g^{-1}$ and C*, with mean diameter of 20 nm and BET-area $= 115\ m^2\,g^{-1}$. The nitrogen gas (AGA Co.) contained 5 p.p.m. O_2 and 5 p.p.m. H_2O. The reactor, a vertical graphite furnace in an autoclave, permitting control of the gas flow (1–$10\ l_{(stp)}\,min^{-1}$) through the sample, was described in Part I [2], as was also the preparation procedure for the mixtures.

TABLE I Compositions of starting materials

Mixture	Raw materials	Weight ratio	Molar ratio
A	α-Al_2O_3/C	3	0.353
B	α-Al_2O_3/C	2/3	0.078
C	γ-Al_2O_3/C	2/3	0.078
D	α-Al_2O_3/C*	2/3	0.078
E	γ-Al_2O_3/C	2	0.235
Stoichiometric ratio		2.83	0.333

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The charges were about 0.7 g "macaroni"-shaped granules (diameter = 1.5 mm, l = 1–6 mm) spread on a perforated graphite foil. A strict temperature programme was followed in all runs, with heating at a constant rate of 20 K min^{-1} up to the plateau temperature, 1500 or 1600 °C, which was controlled to within $\pm$ 1 K. A constant nitrogen pressure, in the range 0.1–5 MPa, was maintained in the reactor during all runs.

The samples were decarburized by heating in air at 700 °C for several hours, prior to characterization by SEM (A Jeol JSM-820 instrument) and surface-area measurement (BET, FlowSorb II 2300, Micromeritics Co). In order to differentiate Al_2O_3 and AlN particles, some samples were subjected to microarea elemental analysis, by use of a Jeol JSM-880 scanning electron microscope equipped with a Link System AN 10000.

3. Results

The microscopic appearance of samples from mixtures containing coarse α-Al_2O_3, run at a high pressure and a low gas-flow rate, 5 MPa and 1 l min^{-1}, was distinct from that of samples run at a lower pressure ($<$ 2 MPa) or a higher gas-flow rate. In the first case, discrete AlN particles formed (Fig. 1c, f and i), smaller with B and D (carbon excess) than with A (alumina excess). In the second case, large aggregates or chains of particles dominated the scanning electron micrographs, and this feature did not change with synthesis time or degree of conversion; 1 or 4 h made no difference (Fig. 1b, d, e, g and h).

Occasionally, whiskers were observed in the samples (Fig. 1a), mostly of mixture A (alumina excess). Particularly, temperatures below 1600 °C and pressures lower than 0.5 MPa seemed to be favourable conditions for AlN whisker formation on the granule surfaces and the supporting graphite foil.

The use of fine γ-Al_2O_3 as starting material is advantageous to reactivity [2], and also to morphology, if discrete, approximately spherical particles are desired. As Fig. 2 shows, samples made up of discrete particles were obtained from mixtures C and E at all pressures and gas flows, ϕ, in the ranges 0.1–5 MPa, 1–10 l min^{-1}. The way that the particle size can be controlled by $\phi(N_2)$ is also quite interesting. With mixtures C and E at 1600 °C (Fig. 2a–g) the AlN grain size was found to vary between ~ 0.5 and 3 µm, the minimum size obtained at the highest gas-flow rate, 10 l min^{-1}. In this respect, the two mixture types seem to be somewhat different, as the minimum size, 0.5 µm was reached with mixture C (larger carbon excess) at 10 l min^{-1} (Fig. 2e), while the smallest particles produced from mixture E were 1 µm (Fig. 2b).

Fig. 2h shows the result of a special run at 5 MPa with the ordinary temperature programme, but a rapid gas flow, $\phi(N_2)$ = 10 l min^{-1}, during heating up and then 1 l min^{-1} for the remaining 4 h at 1600 °C. The grain size became identical ($<$ 1 µm) in this experiment with that obtained at the same $p(N_2)$ and T but constant $\phi(N_2)$ = 10 l min^{-1} (Fig. 2e). In another special run, also with mixture C at 1600 °C and 5 MPa, a slow gas flow, $\phi(N_2)$ = 1 l min^{-1}, was used during the first half hour of the run, then 10 l min^{-1}.

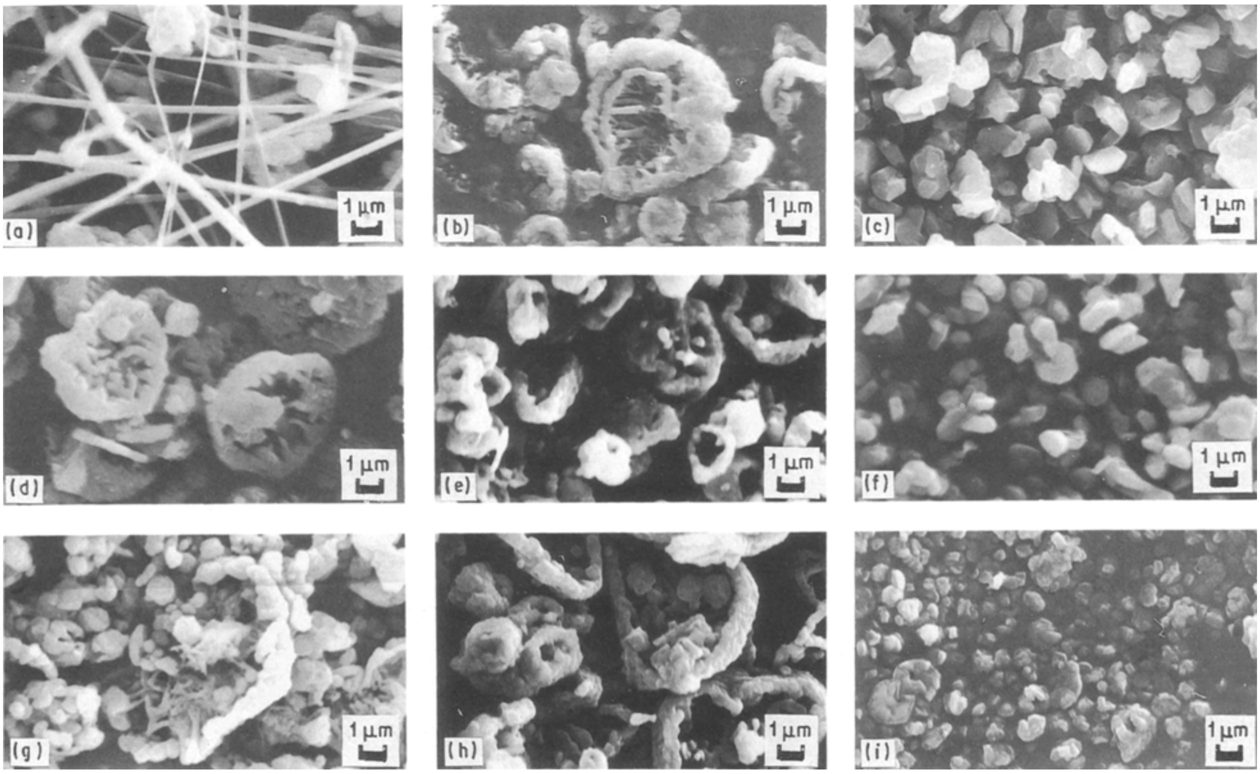

Figure 1 Scanning electron micrographs of samples A, B and D, run at different temperatures, pressures and gas-flow rates and subsequently decarburized by heating in air at 700 °C. (a) A, 1500 °C for 4 h, 0.5 MPa and 1 l min^{-1}, (b) A, 1600 °C for 4 h, 0.5 MPa and 5 l min^{-1}, (c) A, 1600 °C for 4 h, 5 MPa and 1 l min^{-1}, (d) B, 1600 °C for 1 h, 0.5 MPa and 5 l min^{-1}, (e) B, 1600 °C for 4 h, 5 MPa and 10 l min^{-1}, (f) B, 1600 °C for 4 h, 5 MPa and 1 l min^{-1}, (g) D, 1600 °C for 1 h, 1 MPa and 1 l min^{-1}, (h) D, 1600 °C for 4 h, 0.5 MPa and 1 l min^{-1}, (i) D, 1600 °C for 6 h, 5 MPa and 1 l min^{-1}.

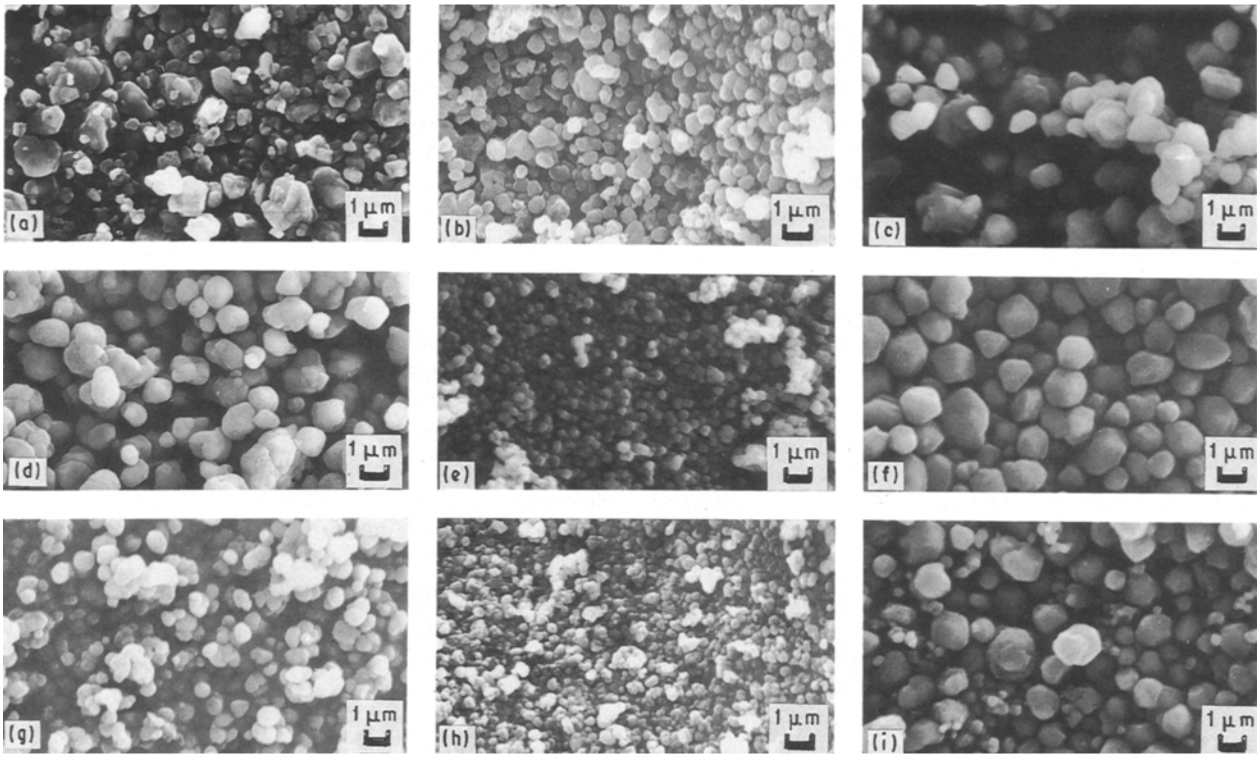

Figure 2 Scanning electron micrographs of samples C and E, run at 1600 °C, different pressures and gas-flow rates for 4 h and subsequently decarburized by heating in air at 700 °C. (a) E, 0.11 MPa and 2 l min^{-1}, (b) E, 5 MPa and 10 l min^{-1}, (c) E, 2 MPa and 1 l min^{-1}, (d) C, 0.5 MPa and 1 l min^{-1}, (e) C, 5 MPa and 10 l min^{-1}, (f) C, 5 MPa and 1 l min^{-1}, (g) C, 2 MPa and 5 l min^{-1}, (h) C, 5 MPa, 10 l min^{-1} during heating and then 1 l min^{-1}, (i) C, 5 MPa, 1 l min^{-1} for 0.5 h and 10 l min^{-1} for 3.5 h.

The coarse-grained product (1–2 µm, Fig. 2i) resembles that of a sample run at a constant low gas flow rate, 1 l min^{-1} (Fig. 2f).

Using a CO (1%)/N_2 mixture as the feed gas during heating-up and then pure nitrogen, a run with mixture C at 1600 °C, 4 MPa produced the powder shown in Fig. 3a, which is coarser than a powder obtained with pure nitrogen under otherwise similar conditions (Fig. 2e). When 2% CO was mixed in the feed nitrogen, the conversion became very low in a 4 h run with mixture C at 1600 °C, as mentioned in Part I [2]. Scanning electron micrographs of such a sample (Fig. 3b) reveal small particles, nitrogen-containing according to microanalysis, mixed with nitrogen-free large particles. These are most likely Al_2O_3, but their mode of formation is unknown so far, as the size (> 1 µm) is much larger than that of the γ-Al_2O_3 starting material. Some of the grains seem to have developed a distinct crystal habit different from that of the original Al_2O_3 particles.

4. Discussion

It is generally believed that two kinds of AlN formation mechanism are operative during carbothermal reduction of alumina in nitrogen; one includes gas-phase reactions, the other proceeds in the solid state. The overall reaction

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g) \qquad (1)$$

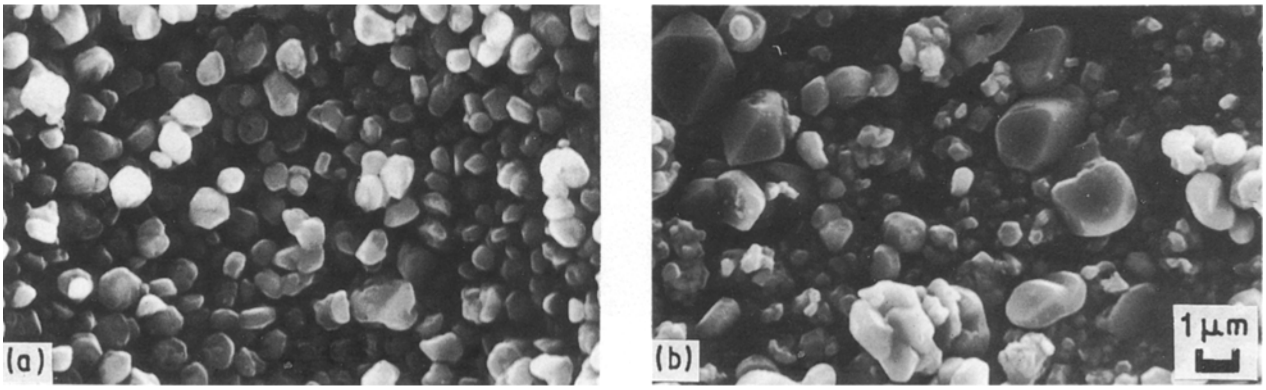

Figure 3 Scanning electron micrographs of sample C, run at 1600 °C, 4 MPa for 4 h in CO/N_2 mixtures: (a) 1% CO, 10 l min^{-1} during heating and then pure nitrogen, (b) 2% CO, 10 l min^{-1} during heating and then 1 l min^{-1}. The samples were decarburized in air.

is expected to proceed via a two-step process, at $T > 1500\,^\circ C$; first the formation of aluminium-containing gas species, such as Al(g) and $Al_2O(g)$

$$Al_2O_3(s) + 3C(s) \rightarrow 2Al(g) + 3CO(g) \quad (2)$$

$$Al_2O_3(s) + 2C(s) \rightarrow Al_2O(g) + 2CO(g) \quad (3)$$

which react subsequently with nitrogen, in the presence of carbon, to produce aluminium nitride, as follows

$$2Al(g) + N_2(g) \rightarrow 2AlN(s) \quad (4)$$

and/or

$$Al_2O(g) + N_2(g) + C(s) \rightarrow 2AlN(s) + CO(g) \quad (5)$$

and/or

$$Al_2O(g) + N_2(g) + CO(g) \rightarrow 2AlN(s) + CO_2(g) \quad (6)$$

followed by

$$CO_2(g) + C(s) \rightarrow 2CO(g) \quad (7)$$

From our SEM results, the morphology of most product powders is seen to be dependent on the choice of the synthesis parameters $p\ (N_2)$ and $\phi(N_2)$ (Figs 1 and 2). Furthermore, the AlN grains do not seem to bear any resemblance to the Al_2O_3 particles in the starting mixtures. These observations suggest that crucial reaction paths proceed via the gas. The occasional formation of whiskers on the surface of the granules and on cooler furnace parts downstream reveal substantial evaporative losses of aluminium-containing species, as mentioned above. Thermodynamic calculations show that the equilibrium partial pressures of species such as Al(g) and $Al_2O(g)$ can reach $\sim 10^2$ Pa under the present experimental conditions [2], and these are the candidate agents for materials transport.

Whiskers are likely to form by heterogeneous nucleation [3], also at a relatively low supersaturation level of aluminium species. This would explain why AlN whiskers are easily formed at relatively low temperatures and nitrogen pressures, particularly for mixture A having an excess of coarse α-Al_2O_3. On the other hand, the uniform crystal size obtained in many of our runs is probably a result of homogeneous nucleation.

If carbothermal AlN formation mainly proceeds by homogeneous nucleation from the gas, the resulting grain size, d_{AlN}, is likely to be a function of the rates of nucleation, R_N, and growth, R_G. It is anticipated that a high growth rate will lead to a restricted number of large particles, while a high nucleation rate will yield numerous small particles.

4.1. Mixtures with fine-grained alumina

At all pressures and gas-flow rates used in this study mixtures C and E, containing fine-grained γ-Al_2O_3, were found to produce discrete particles of uniform and approximately spherical shape (Fig. 2a–i). This supports the view that nucleation and growth mainly occurred by materials transport in the gas, not by solid-state diffusion.

From a comparison between the experiments with changed flow, and the ordinary runs (Fig. 2e, f, h and i), we conclude that the AlN particle formation is essentially complete after the initial synthesis period (0.5 h). Judging from the CO recordings mentioned previously (Fig. 12 in [2]), this is also the "impetuous" period, characterized by vivid CO evolution. After that, there is evidently no appreciable grain growth, in spite of many hours of annealing at 1600 °C.

A comparison between the powder run at 1600 °C, and 4 MPa in an 1% CO–N_2 mixture (Fig. 3a) and a powder run in pure nitrogen, under otherwise similar conditions (Fig. 2e), shows that a high CO level in the reacting gas favours particle growth relative to nucleation. This means, just as for the conversion rate discussed in Part I [2], that the effect of gas-flow rate on product particle size is the result of CO(g) removal from the sample space. A prerequisite for obtaining small AlN particles is, consequently, that p(CO) is suppressed during their formation from aluminium-containing gas species; e.g. by use of a high flow rate of pure nitrogen through the sample holder.

Our results with mixtures C and E thus indicate that the AlN nucleation rate, R_N, is hampered by an increased CO level during the carbothermal reaction. This may be expected from the formulation of Reactions 2 and 3, proposed for production of aluminium-containing species supersaturating the gas, both having CO(g) on the product side. Thermodynamic calculations [2] show that the equilibrium pressures of Al(g) and $Al_2O(g)$, over carbon and Al_2O_3 but in the absence of AlN, are reduced by an increase of p(CO) in the gas. The evaporation rate of these species ought to be proportional to their equilibrium partial pressure. Reaction 5 or the equivalent Reactions 6 + 7 should also be retarded by a p(CO) increase. These processes can be operating both in nucleation and growth, although $p(Al_2O)$ is generally less than p(Al) by a factor of 3–10 (Fig. 7 in [2]) and thus less important.

That an increased C/Al_2O_3 ratio leads to smaller $d_{(AlN)}$ (mixture C compared with E) can be explained by an enhanced rate of Reaction 2, when the reducing capacity of the system is increased, positively affecting R_N. An alternative explanation for the observed variation of $d_{(AlN)}$ with p(CO), i.e. that R_G is stimulated by an increased CO level, is less likely.

4.2 Mixtures with coarse alumina

It is not easy to explain the observed variation in particle size and shape with process parameters for the compositions made with coarse α-Al_2O_3, mixtures A, B and D. The main reason is that we presently do not know which reactions are really involved in nucleation and growth, nor their relative importance at different temperatures and pressures. Of course, this is also true for the previous discussion of mixtures C and E. However, in the case of mixtures A, B and D, a contributing difficulty is that so far we have not been able to reveal the detailed features of the highly agglomerated structures that appear under specific synthesis conditions (Fig. 1). These are a low pressure ($p(N_2) < 5$ MPa) and/or a high gas-flow rate

($\phi(N_2) \gg 1\,l\,min^{-1}$). The agglomerates may be small AlN particles, formed from the gas and making up a dense mass, or they may originate from sintered Al_2O_3 aggregates, which have transformed to AlN by solid state reactions with carbon and nitrogen.

Even so, we wish to suggest processes, including Reactions 2–7 and an unspecified solid-state reaction leading to AlN, which might have brought about the different microstructural characteristics observed in powders A, B and D.

The primary cause for the different behaviour of powders A, B and D, compared to C and E, must be the difference in Al_2O_3 specific surface area. The fact that coarse α-Al_2O_3 tends to produce agglomerated AlN at 1600 °C, 0.5 MPa, may indicate that in this case solid-state reactions between Al_2O_3, carbon and nitrogen dominate over gas phase routes. The formation of discrete particles (Fig. lc, f and i) at 5 MPa (slow gas flow) is possibly due to an increased rate of gas-phase reactions such as Reaction 4 at a higher $p(N_2)$, only partly compensated by the reduced Al(g) activity (Fig. 7 in [2]).

The increased tendency for agglomeration, also at 5 MPa, with an increased gas flow rate up to $10\,l\,min^{-1}$ (Fig. 1e), could be due to an enhancing effect of reduced $p(CO)$ on the rate of the solid-state reactions, which are expected to produce CO(g). To test this assumption, a special run with mixture D at 5 MPa, and a high gas-flow rate of an 0.7% CO + N_2 gas mixture, was performed. The chain-like particle aggregates typical for "high-flow samples" are missing from this powder (Fig. 4), which proves that $p(CO)$ is determinative for the powder morphology, also in case of mixture type A, B or D. However, the CO addition evidently had no effect on particle size in this experiment; the powder consisted of large lumps of non-uniform size and shape. Thus, we have no evidence for a change in AlN formation mechanism with changing $p(CO)$ to explain the observed effect of gas-flow rate.

An alternative explanation of the observed formation of discrete particles in mixture D at high $p(N_2)$ and low gas-flow rates is that under such conditions partial pressures of gaseous aluminium species are not reduced by excessive leakage from the sample space. This means that AlN can form by Reaction 4 from a supersaturated gas, even with a low-surface area Al_2O_3 reactant. If the sample holder is efficiently vented, on the other hand, alternative routes to AlN may dominate: in the solid state or possibly occurring via heterogeneous nucleation from the gas at low supersaturation levels, resulting in lumps of crystals.

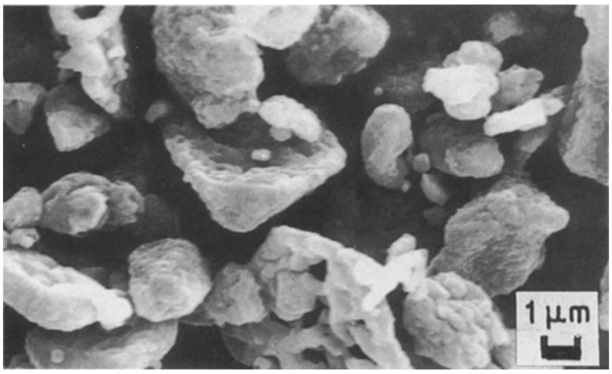

Figure 4 Scanning electron micrograph of sample D, run in 0.7% CO + N_2 at 1600 °C, 5 MPa, $10\,l\,min^{-1}$.

5. Conclusions

In the carbothermal reduction of Al_2O_3 in pressurized nitrogen, AlN powders with different particle morphology can be produced, depending on the choice of the parameters gas-flow rate, pressure and starting material type.

1. Reactant mixtures containing fine-grained γ-Al_2O_3 produce discrete, approximately spherical AlN particles ($< 3\,\mu m$) at $T = 1600\,°C$ over the pressure and gas-flow rate ranges 0.1–5 MPa, 1–$10\,l\,min^{-1}$.
2. When mixtures containing coarse-grained α-Al_2O_3 are run at 1600 °C and pressures < 2 MPa, large aggregates and "chains" of AlN particles form. On the other hand, at a higher nitrogen pressure and a moderate gas-flow rate, discrete AlN particles form, being smaller the larger is the C/Al_2O_3 ratio.
3. An AlN powder with a very small particle size (0.5 µm) can be obtained starting with a mixture of γ-Al_2O_3 and carbon black (BET surface areas 138 and $82\,m^2\,g^{-1}$, respectively) in the molar ratio 0.08, at $T = 1600\,°C$, $p(N_2) = 5$ MPa and $\phi(N_2) = 10\,l\,min^{-1}$.
4. Reactions including aluminium-containing gas species play an important role in AlN particle formation in the carbothermal synthesis.

Acknowledgements

The authors thank Professor Lars Kihlborg for valuable comments on this manuscript, Drs Magnus Ekelund and Kjell Jansson for help with the SEM, and Dr Sven Westman for revising the English of the text. The work has been sponsored by the Swedish Natural Science Research Council and the Swedish Board for Technical Development.

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Received 7 September and accepted 30 October 1992