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Carbothermal synthesis of aluminium nitride at elevated nitrogen pressures

Part I *Effect of process parameters on conversion rate*

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This paper is the first part of an investigation of carbothermal nitridation of alumina at elevated nitrogen pressure. The effect of some process parameters on nitridation rate was studied at different temperatures (1300–1700 °C) and pressures (0.1–5 MPa). The experiments were performed in a graphite furnace permitting a controlled nitrogen flow through the sample holder, and continuous measurement of CO in the outlet gas. The products were characterized by X-ray diffraction, BET and elemental analyses. The nitridation rate was found to be a function of the process parameters. For a suitable temperature and pressure, e.g. 1600 °C and 1 MPa, pure AlN was obtained after just 1 h, with very low residual oxygen content (0.4 wt%). At a high gas-flow rate ($\geqslant 5\ \mathrm{l\,min^{-1}}$), the optimum range of pressure was 0.5–1 MPa at 1550–1700 °C. The nitridation was hampered by even small amounts of CO added to the system. No intermediate phases formed under the experimental conditions studied. Thermodynamic calculations on the Al–O–C–N system were performed in a search for explanations of the results.

1. Introduction

The carbothermal reduction and nitridation (CTN) of aluminium oxide is an important preparation method for high-quality AlN powder. The overall reaction

$$Al_2O_3(s) + 3C(s) + N_2(g) \longrightarrow 2AlN(s) + 3CO(g) \quad (1)$$

is believed to proceed via a two-step process at $T > 1500\,°C$ [1–3]; first the formation of aluminium-containing gas species, such as Al(g) and $Al_2O(g)$

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

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

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

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

and/or

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

and/or

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

followed by

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

Some authors stress the significance of solid–solid interactions between carbon and alumina and thus the importance of a careful mixing procedure for a high overall reaction rate [3, 4].

Generally, desirable properties of nitride and oxide powders, intended for high-performance ceramics, are high purity, small particle size (< 1 μm), narrow size distribution and minimal agglomeration. These requirements seem to be met fairly well by AlN powders prepared by CTN [5]. Thus, a reactive starting mixture, consisting of a colloidally dispersed alumina precursor and a carbon-containing resin, was reported [6] to produce a homogeneous AlN material, with 0.3 μm mean particle diameter and $5\ m^2\,g^{-1}$ surface area, after 6 h in flowing nitrogen at 1575 °C.

A less-sophisticated preparation procedure is wet-mixing/ball-milling of a mixture of carbon and Al_2O_3 powders. It has the merit of simplicity, and has been found to yield relatively fine-grained powders, however usually agglomerated to some extent. A material with mean grain size 0.5 μm was obtained after 5 h heating at 1500 °C of an attrition-milled mixture of high surface-area carbon black ($500\ m^2\,g^{-1}$) and calcined alumina ($9\ m^2\,g^{-1}$) [3]. In this case, 10% AlN powder had been added to the starting mix; such a "seeding" procedure is a common trick in CTN syntheses of Si_3N_4 and AlN and has been found to have a controlling effect on the particle size.

In unseeded samples, the AlN particle size was found to be larger, the higher was the temperature [2].

Suppression of the residual carbon and oxygen contents of the samples is a constant concern for the preparative chemist using CTN. A large carbon excess is normally used in the starting mixtures, as this has

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proved to be beneficial to the conversion. The excess carbon left in the samples is burnt off in air at ~650 °C.

It seems, however, that the oxygen levels reported in papers on laboratory CTN-synthesis experiments are generally relatively high, 2%–3% also for low surface-area materials ($< 5\ m^2\,g^{-1}$), and this is indicative of oxygen being introduced during the decarburization. To be able to take full advantage of the excellent intrinsic thermal conductivity of AlN, e.g. for use in electronic devices, one must reduce the residual oxygen content in the powder [5]. The low oxygen values specified for some exclusive commercial AlN materials have probably been obtained by post-treatment procedures, e.g. purification by means of a reactive gas.

The present work is the first part of an investigation of CTN of Al_2O_3 at elevated nitrogen pressure. It was undertaken in order to study the effect of an increased nitrogen pressure on the conversion to AlN. A subsequent paper [7] will discuss the combined effects of pressure and other process variables, such as gas-flow rate, on the size and shape of the AlN particles.

2. Experimental procedure

2.1. Starting materials

Four solid reagents were used as raw materials: coarse α-Al_2O_3, fine γ-Al_2O_3 and two kinds of carbon black. Their physical and chemical characteristics are listed in Table I. The fine γ-Al_2O_3 was a poorly crystallized decomposition product of ammonium alum. The nitrogen gas ("Nitrogen PLUS", AGA Co., Lidingö, Sweden), with impurities $O_2 < 5$ p.p.m. and $H_2O < 5$ p.p.m., was used without further purification. Gas mixtures of carbon monoxide and nitrogen of the same purity were used in some experiments.

The starting materials were five mixtures of alumina and carbon black powders, denoted A, B, C, D, and E in Table II.

TABLE I Properties of raw materials

Reagent	Grain size	BET surface (m^2g^{-1})	Source, grade
α-Al_2O_3	1–10 μm	0.55	Fisher Scientific Co., A-591
γ-Al_2O_3	< 1 μm	138	made in-house
C	~30 nm	82	Nordisk Philblack Co., N330
C*	~20 nm	115	Nordisk Philblack Co., N220

TABLE II Compositions and theoretical relative weight change of starting materials

Symbol	Weight ratio	Molar ratio	$-\Delta m/m_0$ for complete conversion (%)
A	α-Al_2O_3/C = 3	0.353	38.8
B	α-Al_2O_3/C = 2/3	0.078	22.0
C	γ-Al_2O_3/C = 2/3	0.078	22.0
D	α-Al_2O_3/C* = 2/3	0.078	22.0
E	γ-Al_2O_3/C = 2	0.235	36.6
Stoichiometric ratio	2.83	0.333	40.6

Every composition was homogenized by milling an ethanol slurry in a plastic bottle with SiAlON balls for 4 days. The slurry was subsequently dried to a plastic mass and then pelletized to granules (diameter = 1.5 mm, length = 1–6 mm). These were further dried to remove the alcohol prior to charging into the autoclave.

2.2. Apparatus

The carbothermal nitridation of alumina at elevated nitrogen pressure was performed in a gas autoclave with a vertical graphite furnace (Fig. 1). The furnace tube and sample holder (Fig. 2) were made of a pure graphite material and designed so that the nitrogen gas introduced into the autoclave was forced through the charge and then the shortest way out via a reducing valve and a flow meter.

The nitrogen flow rate, ϕ, and pressure, p, in the autoclave were in the range 0.5–25 $l_{(stp)}\,min^{-1}$ and 0.1–5.0 MPa, respectively. The carbon monoxide content in the outlet gas was continuously measured by means of an infrared detector (Leco Corp., Svenska AB, Sundbyberg, Sweden). The sample temperature was measured with a W–Re thermocouple, calibrated against the melting points of gold, palladium and platinum. The maximum deviation of the measured temperature from the actual value was found to be within ± 5 K, while the plateau temperature could be kept within ± 1 K.

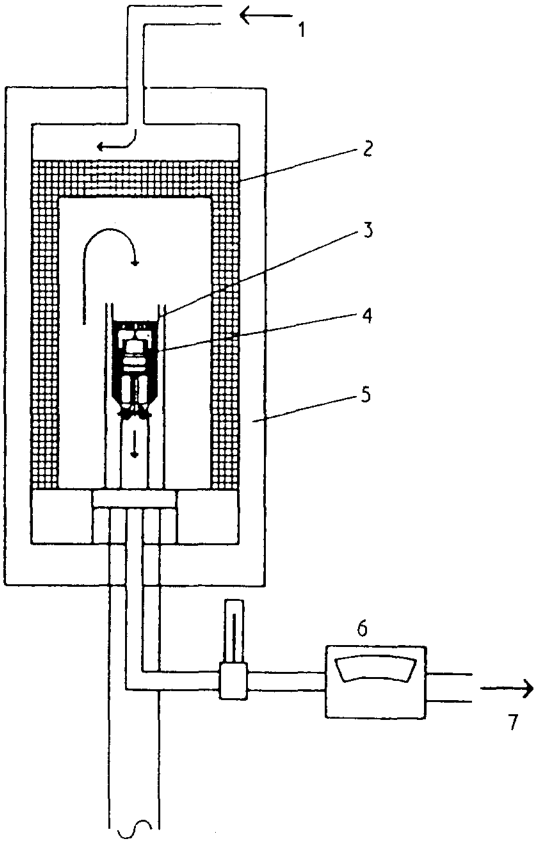

Figure 1 The autoclave with the graphite furnace. 1, Gas inlet; 2, thermal insulation; 3, furnace tube; 4, sample holder; 5, pressure vessel; 6, IR detector (CO); 7, gas outlet.

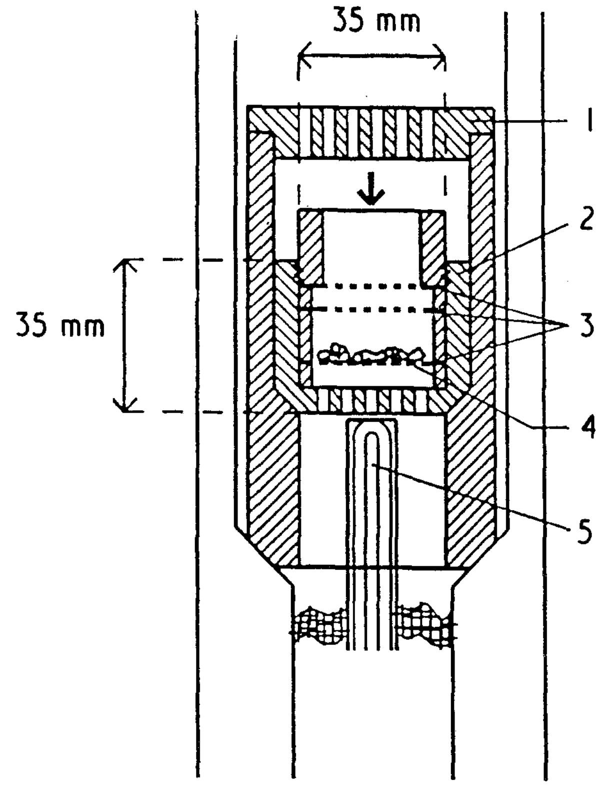

Figure 2 The sample holder (graphite). 1, perforated lid; 2, sample holder with screw ring; 3, perforated graphite foils and spacer rings; 4, sample; 5, Al_2O_3 and graphite thermocouple shielding tubes.

2.3. Synthesis procedure

A charge of about 0.7 g was used in every run and spread on a perforated graphite foil in the sample holder. In order to eliminate oxygen from the autoclave before reduction, the autoclave was flushed several times with nitrogen (1 MPa) at room temperature and three times during heating (at about 200, 400 and 600 °C).

A standardized temperature programme, controlled by a PID regulator, was followed in all runs: rapid heating at a rate of $20\ K\,min^{-1}$ to a plateau temperature, holding at this level and then cooling at $30\ K\,min^{-1}$. The exact time of opening of the gas outlet valve was not important for the degree of conversion below 1300 °C. Normally the gas outlet valve was opened at 1100 °C on heating and closed at 1400 °C on cooling. Residual carbon in the reacted samples was removed by heating in air at 700 °C for 5–22 h.

2.4. Characterization

Phase analysis of the experimental products was performed by X-ray powder diffraction (Guinier–Hägg-type focusing cameras). The oxygen, carbon and nitrogen contents were determined by an independent laboratory, using a fusion–gas analysis method. Carbon was also determined by thermogravimetry ("TGS-2", Perkin–Elmer Co.) in an oxygen atmosphere. Surface areas of the samples were determined by the BET method ("FlowSorb II 2300", Micromeritics Co.).

2.5. Thermodynamic calculations

In order to explain some of the experimental results, free-energy minimization calculations on the system Al–O–C–N were performed. The computer program SOLGASMIX [8] was used. We have considered product mixtures containing 34 different gas species as well as 7 condensed phases (Al, C, AlN, α-Al_2O_3, γ-Al_2O_3, Al_4C_3 and Al_4O_4C). The gas phase was regarded as ideal. All ΔG_f° data were taken from the JANAF Thermochemical Tables except those of Al_4O_4C which was taken from Frank *et al.* [9].

3. Results

The carbothermal reduction rate was found to be very sensitive to the reaction temperature, corroborating earlier studies [1, 2]. The experimental results demonstrated that aluminium nitride begins to form slowly at 1300 °C. The rate of reduction grows markedly with increase in temperature up to 1400 °C, then sharply increases at about 1500 °C. This is shown in Fig. 3, where the relative weight change (RWC), $\Delta m/m_0$ (m_0 is the charge weight), is used as a measure of conversion.

Figs 4–6 show the resulting degrees of conversion versus gas-flow rate or nitrogen pressure in a number

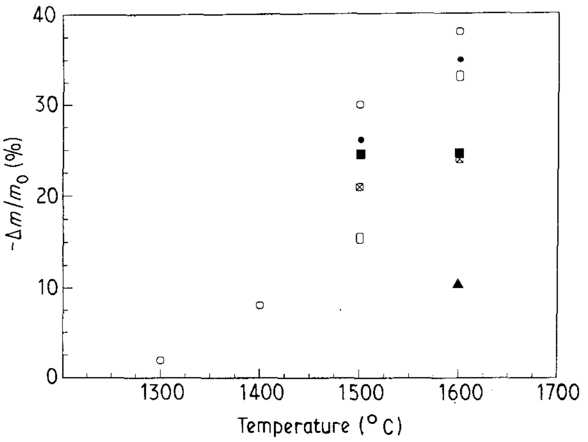

Figure 3 Conversion ($-\Delta m/m_0$) as a function of temperature for 4 h runs at different $p(N_2)$ and $\phi(N_2) = 1\ l\,min^{-1}$ with different starting mixtures. Full conversion corresponds to: A, $-\Delta m/m_0 = 38.8\%$; C, $-\Delta m/m_0 = 22.0\%$; E, $-\Delta m/m_0 = 36.6\%$. (▲) C, 4 MPa, N_2 + 2% CO; (●) E, 0.5 MPa; (☒) C, 5.0 MPa; (■) C, 0.5 MPa; (▯) A, 5.0 MPa; (○) A, 0.5 MPa.

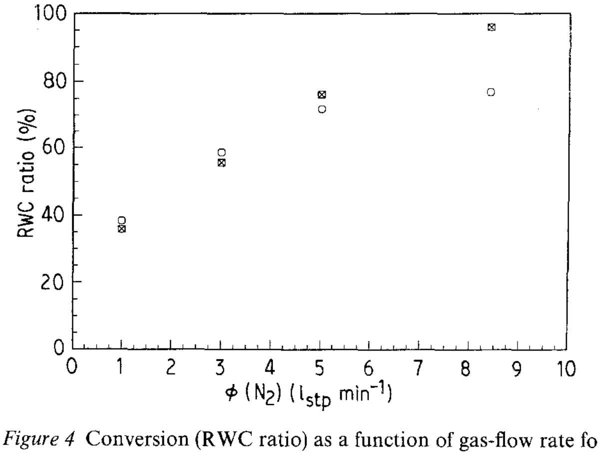

Figure 4 Conversion (RWC ratio) as a function of gas-flow rate for 1 h runs at 1500 °C and 0.5 MPa with starting mixtures (○) B and (☒) E. The RWC ratio is defined as the observed relative weight change (RWC, $-\Delta m/m_0$) divided by the maximum RWC, calculated for full conversion.

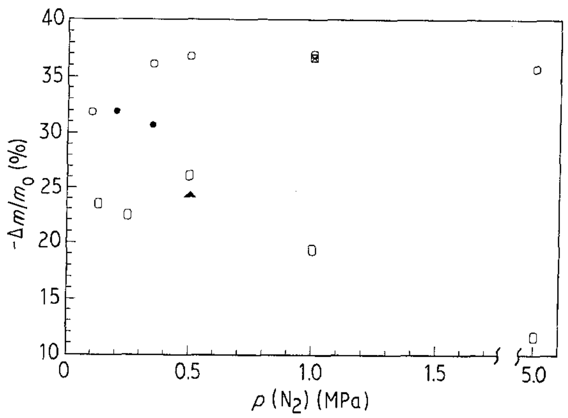

Figure 5 Conversion as a function of nitrogen pressure for 1 h runs at 1600 °C and different gas-flow rates with starting mixture A. Full conversion corresponds to $-\Delta m/m_0 = 38.8\%$. Flow rate (l min^{-1}): (☒) 10, (○) 5, (●) 3, (☐) 1, (▲) 1, N_2 + 1% CO.

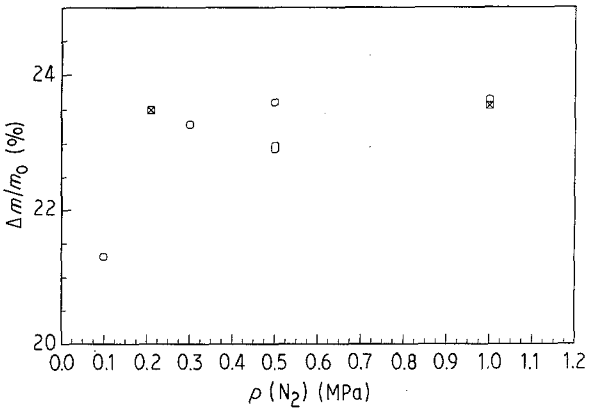

Figure 6 Conversion as a function of nitrogen pressure for 1 h runs at 1600 °C and different gas-flow rates, with starting mixture B. Flow rate (l min^{-1}): (○) 5, (☒) 2–3, (☐) 1.

of nitridation runs. These results were obtained under conditions giving a somewhat lowered conversion rate, i.e. at low temperature and for a short time or with a relatively high Al_2O_3/C ratio. Here the yield was found to increase with gas-flow rate up to a certain level, and also with nitrogen pressure in runs with high gas flows. If low gas-flow rates were used, an increase of pressure apparently had a negative influence on the conversion rate (Fig. 5).

The relative weight change, RWC, is but a rough measure of conversion; in fact it can be misleading, as RWC is not exclusively due to CO losses following Reaction 1, but also partly to irreversible evaporative losses of aluminium-containing species, such as Al(g) and Al_2O(g). This can be inferred from mass-balance calculations based on accurate nitrogen, oxygen and carbon analyses and also from observations that, under certain conditions, AlN whiskers form in the furnace during the carbothermal synthesis, downstream from the sample.

Fig. 7 gives the calculated partial pressures of aluminium and Al_2O in N_2 + CO gas mixtures equilibrated with carbon and Al_2O_3 at different pressures and CO contents.

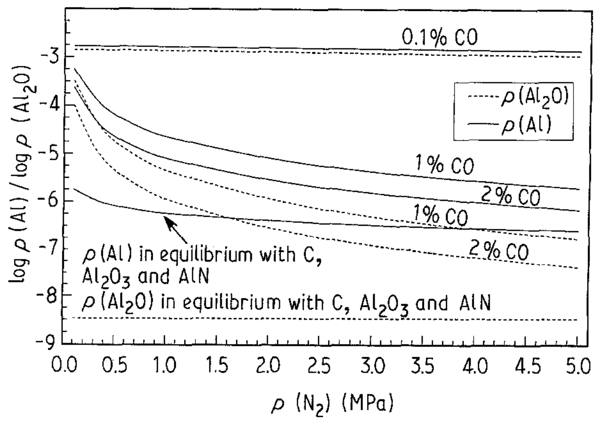

Figure 7 Calculated partial pressures (bar) of aluminium and Al_2O in (supersaturated) mixtures of carbon and Al_2O_3, equilibrated with nitrogen atmospheres of different CO contents and at different pressures. Shown also (——) p(Al) and (- - -) p(Al_2O) in equilibrium with carbon, Al_2O_3, AlN and the gas.

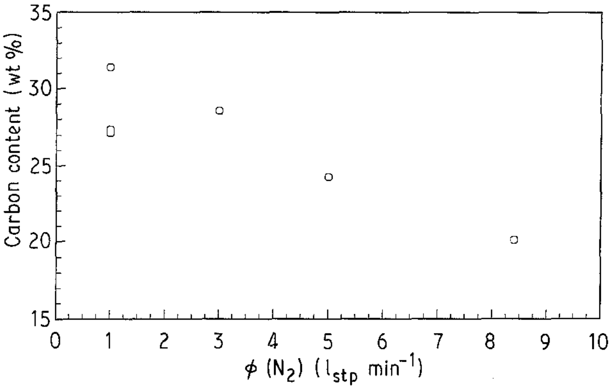

Figure 8 Residual carbon contents in samples of starting mixture E, run for (○) 1 and (☐) 4 h at 1500 °C, 0.5 MPa and different gas-flow rates.

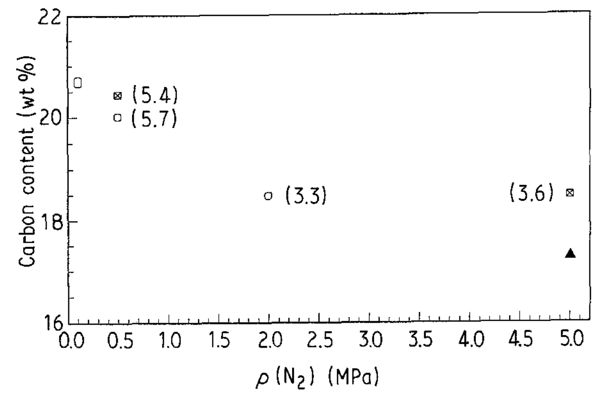

Figure 9 Residual carbon contents in samples of starting mixture E, run for 4 h at 1600 °C, different gas-flow rates and nitrogen pressures. Figures in parentheses are the oxygen values calculated for decarburized samples. Flow rates (l min^{-1}): (▲) 10, (☒) 5, (☐) 2, (○) 1.

More appropriate measures of conversion, particularly in highly reacted samples, are the residual carbon and oxygen contents. The resulting carbon values after 1 h runs with mixture E in Fig. 4 are shown in Fig. 8, which once again illustrates the positive flow-rate dependence of conversion. Fig. 9 shows the residual carbon and oxygen contents after 4 h runs at 1600 °C with mixture E and different flow rates. Fig. 10 shows the residual carbon values in the 1 h runs in Fig. 5, with A at 1600 °C, proving that there is a positive dependence of conversion on nitrogen pressure, provided sufficiently high gas flows (5 l min^{-1}) are used.

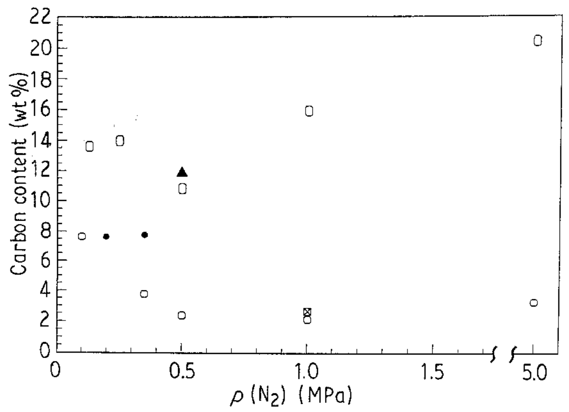

Figure 10 Residual carbon contents in samples of starting mixture A, run for 1 h at 1600 °C, different gas-flow rates and nitrogen pressures. Flow rate (l min^{-1}): ⊠ 10, (○) 5, (●) 3, (⊡) 1, (▲) 1, N_2 + 1% CO.

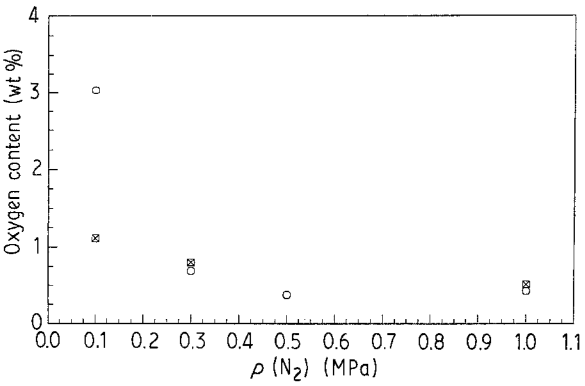

Figure 11 Residual oxygen contents in samples of starting mixtures (○) B and (⊠) D, run at 1600 °C, 5 l min^{-1} and different nitrogen pressures, B for 1 h and D for 4 h.

For mixtures B, C and D, with a large carbon excess, the residual oxygen content is the most sensitive measure of conversion, as well as a parameter of technological importance. Fig. 11 shows the oxygen values, corresponding to the RWC data in Fig. 6, for B samples run 1 h at 1600 °C and $\phi(N_2) = 5\,l\,min^{-1}$. In the same diagram are plotted oxygen figures after 4 h with mixture D at 1600 °C. Evidently, the residual oxygen levels in these samples were suppressed by an increased nitrogen pressure in the range 0.1–0.5 MPa.

Surface areas between 2 and 3 $m^2\,g^{-1}$ were measured for completely reacted samples, after removal of excess carbon by heating in air at 700 °C.

The nitridation proceeds relatively rapidly for the samples with large carbon excess (B, C and D); aluminium nitride and carbon were the only phases in the products after 1 h runs at 1600 °C and a suitable nitrogen pressure, even using small gas-flow rates. After 4 or 6 h heating the residual oxygen content was 0.3%, which seems to be the minimum value. The corresponding figure, calculated for a carbon-free sample is 0.7%. Decarburization would increase the oxygen content slightly.

With mixture E, of lower carbon excess, it took a long time to reach full conversion. Even a 4 h run at 1700 °C, 5.0 MPa and 5 l min^{-1}, yielded a mixture of unreacted α-Al_2O_3 together with AlN and carbon, unless a very large gas-flow rate was used (10 l min^{-1}).

Mixture A was substoichiometric with respect to carbon, and so exhibited a relatively slow reaction rate. The only solid product phases found in samples run at 1500 and 1600 °C were carbon, Al_2O_3 and AlN. No trace of oxynitride was ever detected, even after very short holding times (0–0.5 h). Transient "AlON" formation has been reported to occur [10] under similar conditions, though.

A convenient way to follow the carbothermal reduction is to monitor continuously the concentration of carbon monoxide in the outlet gas. Fig. 12 shows the CO amounts given off by an A sample at $p(N_2) = 0.5$ MPa, 1600 °C and $\phi(N_2) = 1$ and $5\,l\,min^{-1}$ with a typical temperature programme. One can note that the CO level, after a fairly sharp maximum when the plateau temperature is reached, stays relatively high for about half an hour, and then gradually decreases.

A few experiments with N_2/CO gas mixtures have also been made. A retarding effect on the nitridation rate was found, even with additions as small as 1% CO to the N_2 gas, as seen in Figs 3 and 5.

As Reaction 1 is reversible, the concentration of carbon monoxide in the system controls the nitridation rate to a large extent. The p(CO) values limiting AlN formation from C + Al_2O_3 in nitrogen at different pressures and temperatures are shown in Fig. 13, based on thermodynamic calculations with the SOLGASMIX program. Shown are the maximum values

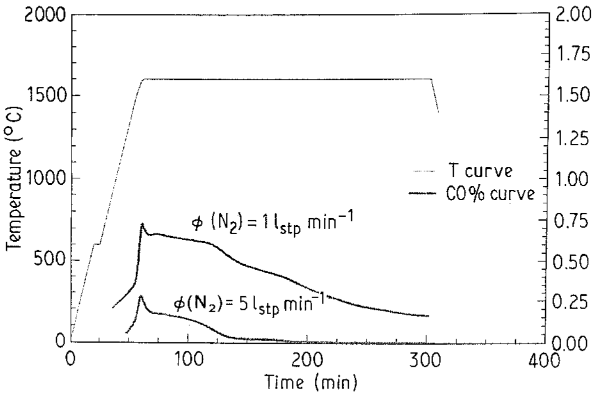

Figure 12 Typical curves of the temperature programme and CO contents of outlet gas in runs with starting mixture A at 1600 °C for 4 h, $p(N_2) = 0.5$ MPa and $\phi(N_2) = 1$ and $5\,l\,min^{-1}$.

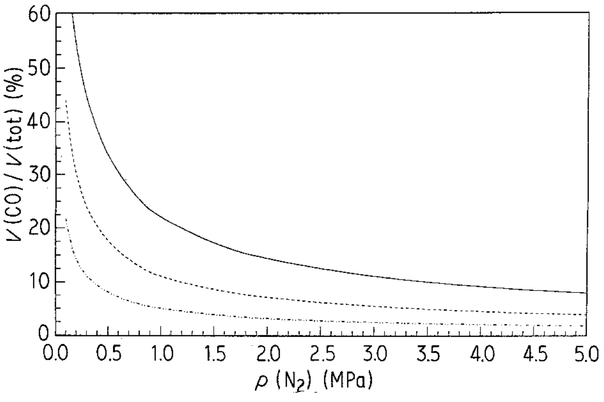

Figure 13 Curves indicating the maximum CO contents in nitrogen for stable coexistence of AlN with carbon and α-Al_2O_3 at (- - — - -) 1500, (– – –) 1600 and (——) 1700 °C and different pressures.

of V_{CO}/V_{tot} in equilibrium with solid AlN, α-Al_2O_3, carbon and the gas for different nitrogen pressures and temperatures. Aluminium nitride cannot form in the area above each curve. Obviously, the carbothermal nitridation is more sensitive to the concentration of carbon monoxide, the lower the temperature and the higher the pressure.

4. Discussion

The continuous CO recordings (Fig. 12) revealed that $p(CO)$ in the outgoing gas may rise to more than 1% p_{tot} for a considerable period (an hour) in a typical run with moderate $\phi(N_2)$. Deliberate addition of 1% CO to the feed nitrogen in a 1 h run with A at 1600 °C, 0.5 MPa and 1 l min^{-1} did not appreciably reduce the conversion (Fig. 11), compared to an ordinary run. Therefore, we conclude that the CO content inside the reacting granules during the introductory period of synthesis will reach higher values than 1%, maybe close to the calculated upper limit in Fig. 13. With 2% CO added to mixture C at 1600 °C, 4.0 MPa, AlN was found to have formed after 4 h, but unreacted Al_2O_3 was in large excess in the sample, and the relative weight change rated at only 10%.

A high gas-flow rate means more efficient removal of carbon monoxide from the sample space. It is clear that flows about 5 l min^{-1} are needed with a 1 g charge in order to eliminate the influence of gas-flow rate on the conversion rate in the present experimental apparatus at 1600 °C and $p(N_2) = 0.1$–1 MPa (Figs 5 and 10). The results in Figs 4 and 8 suggest that still higher flow rates, in excess of 10 l min^{-1}, must be used to make the rate of AlN formation flow-independent at 1500 °C, 0.5 MPa. This can be understood from the thermodynamic calculations (Fig. 13), implying that the barrier to AlN formation, set up by a specific CO concentration in the gas, will increase when the temperature decreases and/or the total pressure increases. A consequence of this is the decrease of conversion with increasing pressure from 0.5–5 MPa, observed in 4 h runs at 1500 °C and a low gas-flow rate with mixtures A and C (Fig. 3). Such a change with pressure was also found for A mixtures at 1600 °C (Fig. 5), while nitridation in the more reactive C mixtures evidently had gone to completion within 4 h at 1600 °C, even at 5 MPa and 1 l min^{-1} (Fig. 3).

However, superimposed on this negative pressure effect on conversion, active via the $p(CO)$ dependence, is also a positive dependence of the overall nitridation rate on the nitrogen pressure. This becomes evident when the screening effect of $p(CO)$ is eliminated by use of sufficiently high gas-flow rates. In short runs (1 h) with mixture A at 1600 °C and $\phi(N_2) = 5$ l min^{-1}, a marked increase in conversion was found with increasing $p(N_2)$ from 0.1–0.5 MPa (Figs 5 and 10). Even the reactive mixture B, which is almost fully converted after 1 h at 1600 °C and 0.3 MPa in gas flows of only 2–3 l min^{-1}, turned out to be less nitrided at atmospheric pressure but otherwise similar conditions (Fig. 11).

The observed effect of nitrogen pressure on the residual carbon and oxygen levels could be due to more favourable kinetics for reactions such as 4, 5 and 6 at higher $p(N_2)$. A shift of equilibrium between solid oxygen-, carbon- and nitrogen-containing phases is also a possibility. In order to clarify the phenomenon in the future, a primary task should be to find out what are the host phases for carbon and oxygen during the final stage of nitridation. Are these phases still unreacted carbon and alumina, or are they transient carbides or oxynitrides?

In the present work, no systematic assessment has been made of the relative reactivities associated with different reactant types and C/Al_2O_3 ratios. We can state though, like previous authors [1, 3], that a large carbon excess promotes nitridation. This raises the question whether a stoichiometric $C + Al_2O_3$ mixture can be fully converted to AlN within reasonable time, at 1600–1700 °C. An incentive for using stoichiometric starting mixtures is to obviate the need for subsequent removal of extra carbon in the samples by heating in air, as such a procedure is likely to introduce some oxygen in the AlN powder. Our results for E mixtures, demonstrated the relative inertness of this composition, compared with the more carbon-rich B, C and D, and so prospects did not seem very bright for a stoichiometric mixture. However, the conversion rate in A, which is understoichiometric with respect to carbon, was not extremely low, and an increased $p(N_2)$ had a large impact on conversion at 1600 °C for both A and E (Figs 5 and 9). Furthermore, successful attempts to prepare AlN from stoichiometric $C + Al_2O_3$ mixtures by long-term heating in atmospheric nitrogen have been reported [11].

Indeed, the result of a single synthesis experiment by the present authors, using a mixture of carbon and α-Al_2O_3 (Table I) in strictly stoichiometric proportions, and prepared in the same simple way as the ordinary mixtures A–E, turned out to be promising. After 8 h at 1600 °C, 0.5 MPa and 5 l min^{-1} a remarkably pure AlN powder was obtained with just 1.0% residual oxygen. Apparently continued synthesis experiments with stoichiometric $C + Al_2O_3$ mixtures in pressurized nitrogen are worthwhile, with the aim of finding an optimal set of process parameters (T, $\Delta T/\Delta t$, $p(N_2)$, $\phi(N_2)$, . . .) for the preparation of a powder with minimal oxygen and carbon contents.

The difference in reactivity found between samples B and C, with coarse α-Al_2O_3 and fine-grained γ-Al_2O_3, respectively, was not great. Nor did the use of different carbon powders (a coarser one in B and a finer one in D) cause any appreciable difference in conversion rate between these mixture types; other parameters, such as $p(N_2)$ and $\phi(N_2)$ turned out to be decisive. For practical purposes, carbon black with a BET area 82 m^2 g^{-1} seems to be fine enough for nitridation of coarse α-Al_2O_3 (0.55 m^2 g^{-1}).

5. Conclusions

1. In the carbothermal preparation of AlN, starting with mixtures of Al_2O_3 and carbon powder, the conversion rate was found to increase with increasing temperature, in the range 1400–1700 °C, and gas-flow rate up to 5 l min^{-1}.

2. At a high gas-flow rate, the degree of conversion, either expressed as the relative weight change or the residual carbon and oxygen contents of a sample, was enhanced by an increase in pressure in the range 0.1–1 MPa.

3. The AlN formation was hampered by even small amounts (a few per cent) of CO added to the nitrogen reactant gas, as predicted from thermodynamic considerations. This hampering effect is more serious the lower the reaction temperature and the higher the total pressure.

4. With starting mixtures of even fairly coarse-grained Al_2O_3 and carbon powders in the mole ratio 1/13, the reaction to AlN went virtually to completion after 4 h at 1600 °C and $p(N_2) = 0.5$ MPa. The oxygen content of such a powder, having a carbon excess, was 0.3 wt % and the BET surface area (of AlN) was $\sim 3\ m^2\ g^{-1}$.

5. A stoichiometric $C + Al_2O_3$ mixture yielded an AlN powder with only 1.0 wt % residual oxygen, after 8 h heating at 1600 °C, 0.5 MPa.

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