Journal of the European Ceramic Society **15** (1995) 1087–1100

0955-2219/95/$9.50

0955-2219(95)00078-X

Carbothermal Synthesis of Aluminium Oxynitride (ALON) Powder: Influence of Starting Materials and Synthesis Parameters

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(Received 6 February 1994; revised version received 9 May 1995; accepted 16 May 1995)

Abstract

Carbothermal synthesis of cubic aluminium oxynitride (ALON) have been performed in a graphite furnace at different temperatures (1700–1860°C) and pressures (0.1–10 MPa). The products were characterized by XRD, SEM and elemental analyses, and the overall compositions were determined by reoxidation in air. The control of excess nitridation was a crucial task in the preparation of ALON. A two-step procedure, first annealing at about 1550°C then at about 1800°C, was found to be effective to this end. CO additions to the N_2 *gas stimulated ALON formation, but a pressure increase resulted in a lower nitridation rate. The particle size and morphology of ALON depended on raw material type and synthesis parameters such as temperature program, pressure, CO content in the* N_2 *gas, and sample compartment type. Thermodynamic calculations in the Al–O–C–N system have been performed in order to explain the experimental results.*

1 Introduction

The acronym 'ALON' is used for an aluminium oxynitride, of composition $Al_{(64+x)/3}O_{(32-x)}N_x$ ($0 \leq x \leq 8$)[1] — a pseudo-binary solid solution of AlN in Al_2O_3, which may be regarded as a nitrogen-stabilized cubic γ-Al_2O_3 phase (spinel). It has interesting optical, mechanical and chemical properties, making it potentially useful as a high-performance ceramic material.

There is some controversy in the literature as to the extent of solid solubility. McCauley and Corbin[2] found the ALON field to range from about 27 to 40 mol% AlN, with fairly constant limits in the temperature range 1700 – 2000°C. They reported the lattice parameter of the cubic structure, in samples quenched from 1975°C, to vary from 7.938 Å for the most oxygen-rich composition to 7.951 Å at the other extreme. According to Lejus,[3] on the other hand, the ALON solid solution extends from about 16 to 33 mol% AlN at 1700°C, and the cell edge varies between 7.927 and 7.950 Å. In a recent study Willems *et al.*[4] established that the homogeneity range is 19–34 mol% AlN at 1850°C, becoming successively more narrow at lower temperatures, reaching zero at 1640°C.

In a comprehensive article by Corbin,[5] the physical properties of ALON are reviewed, and also various preparation methods employed since the first paper on the compound in 1959.[6] A tentative phase diagram of the AlN–Al_2O_3 system is presented, valid at 1 bar of nitrogen pressure. In total, thirteen different oxynitride phases have been reported to date. ALON is the only stable binary phase below 1900°C although other oxynitride or nitrogen stabilized alumina phases are apt to form also in this regime under specific synthesis conditions.[7,8]

Of the ALON synthesis methods tried so far, those demanding the highest temperatures (> 1500°C) are: direct reaction of an alumina + aluminium nitride powder mixture, and reduction/nitridation of alumina with carbon, aluminium metal or hydrogen in nitrogen or ammonia. Oxidation/nitridation of aluminium in air has been used at ca. 1500°C, and the gas phase reaction between aluminium chloride and ammonia is effective below 1000°C.

Carbothermal nitridation of alumina, according to:

$$\left(\frac{64+x}{3}\right)Al_2O_3 + 3xC + xN_2(g) \rightarrow$$
$$\rightarrow 2Al_{(64+x)/3}O_{(32-x)}N_x + 3xCO(g) \quad (1)$$

is a well established preparation procedure for ALON. Several patents have been issued, some of them describing a two-step heat-treatment process in a nitrogen atmosphere; first at 1500–1600°C, then at 1700–1800°C.[9]

The synthesis of ALON powder according to the reaction (1) might seem straightforward but control of the product stoichiometry may be a difficult task. There are several reasons for this. Firstly, at the very high preparation temperatures required, around 1800°C, evaporative losses of aluminium and aluminium suboxides from the charge are likely to be high, particularly in a dynamic atmosphere. Secondly, the reducing conditions prevailing in a graphite furnace, which is a convenient reactor type, may have a large influence on the final O/N ratio in the powder, as was early recognized.[6] Willems *et al.*[10] calculated the composition (oxygen, carbon and nitrogen activities) of the gas phase in stable coexistence with ALON, and concluded that it should be extremely difficult to prepare pure ALON in a flowing N_2 atmosphere without partial reduction or oxidation to AlN or Al_2O_3. A contributing difficulty is that we presently do not know the exact ALON formation mechanism: is it mainly a solid state reaction between aluminium nitride and alumina, or are there important reaction steps occurring *via* the gas? The relatively slow advancement of the ALON formation, even at high temperatures; and observations such as those of Ish–Shalom,[11] that the relative amount of ALON in the product mixture goes through a maximum at a certain annealing time, favour the view that ALON formation is mainly controlled by solid state diffusion. On the other hand, the high activities expected for some aluminium-bearing gas species at the reaction temperatures make it necessary to consider also gas phase reaction steps. Lefort and Billy[12] have suggested that AlN forms on the surface of the Al_2O_3 grains by nitridation of Al vapour, and that ALON subsequently forms at temperatures above ca. 1600°C as a result of solid–solid interactions at the Al_2O_3/AlN interface.

The main purpose of the present investigation of ALON synthesis, by carbothermal nitridation of alumina, was to study the effect of variation of different synthesis parameters on conversion rate, sample stoichiometry and particle morphology, and to elucidate the optimal conditions for synthesis of a monophasic ALON powder in a graphite furnace. To this end, powder mixtures of different alumina and carbon starting materials were heat-treated according to different temperature programs and annealed at 1700–1860°C in flowing nitrogen. Of particular interest was to find out if the nitrogen pressure could be a useful synthesis parameter, as previously found to be the case with Si_3N_4[13] and AlN.[14,15]

2 Experimental

2.1 Sample preparation

Raw materials were alumina and carbon black ('N330', Nordisk Philblack AB, Malmö, Sweden), having a surface area of 82 m^2 g^{-1} and a mean particle diameter = 30 nm. Alumina materials used were coarse α-Al_2O_3 ('A-591', mean particle diameter 5 μm, Fisher Scientific Co., New Jersey, USA) and fine γ-Al_2O_3 (made in-house), with a surface area of 0.6 and 138 m^2 g^{-1}, respectively. The latter was a poorly crystallized decomposition product of ammonium alum. Aluminium nitride ('Grade A', Hermann C. Starck Berlin Gmbh, Goslar, Germany) was used in some comparison experiments. The nitrogen gas ('Nitrogen Plus', AGA Co., Lidingö, Sweden), specified to contain < 5 ppm O_2 and < 5 ppm H_2O, was used without further purification. An N_2 + 10% CO mixture of the same purity level and Ar ('Argon 4.8', AGA Co., Lidingö, Sweden) were used in some experiments.

Starting materials were seven mixtures of alumina and carbon black powders, denoted 'A' – 'G' (Fig. 1). Besides, 'H' was a mixture of Al_2O_3 and AlN, while 'I' was prepared from $AlCl_3 \cdot 6H_2O$ and starch by a sol–gel procedure. Their compositions, theoretical relative weight changes for full conversion and modes of preparation are given in Table 1. The water contents of the aluminas have been compensated for in these calculations.

Three charge types were used: powders, pellets and granules. Powders were obtained by drying an ethanol slurry, milled in a mortar or in a plastic bottle with SiAlON balls for 4 days. About 0.5 g of the dried, yet plastic powders was pressed into cylindrical pellets of 11 mm diameter and 4–8 mm thick, using a pressure of 840 MPa for 30 s. Granules of diameter 1.5 mm and length 1–6 mm were formed by extrusion. Residual alcohol was subsequently removed by further drying.

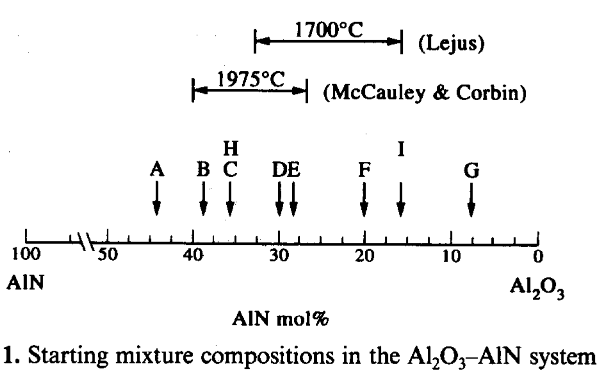

Fig 1. Starting mixture compositions in the Al_2O_3–AlN system. ALON homogeneity ranges suggested by previous authors (Refs 2, 3, and 4) are indicated.

Table 1. Compositions and theoretical relative weight changes of starting mixtures

Symbol	*Wt. ratio*	*Composition (mol% AlN)*	$(-\Delta m/m_0)_{theo.}$ (%)	*Mixing by*
A	α-Al_2O_3/C = 10·0	44·2	14·1	Ball milling
B	γ-Al_2O_3/C = 12·3	38·5	14·1	Milling in mortar
C	α-Al_2O_3/C = 13·0	35·7	11·1	Ball milling
D	γ-Al_2O_3/C = 16·0	29·9	11·3	Ball milling
E	α-Al_2O_3/C = 17·0	28·6	8·6	Ball milling
F	α-Al_2O_3/C = 25·4	20	5·9	Ball milling
G	α-Al_2O_3/C = 70·4	7·7	2·2	Milling in mortar
H	γ-Al_2O_3/AlN = 4·5	35·7	0	Milling in mortar
I	Al_2O_3/C = 33·4	15·7	8·2	Sol–gel procedure

2.2 Synthesis procedure

The carbothermal nitridations of alumina at different nitrogen pressures (0.1–10 MPa) were performed in a gas autoclave with a vertical graphite furnace, described previously.[13,14] The granules or pellets were placed in a graphite sample holder, some of them with a BN (ABB Cerama, Robertsfors, Sweden) liner. Powders were charged in alumina or molybdenum crucibles in the sample holder.

In order to eliminate air from the autoclave before nitridation, the autoclave was flushed several times with nitrogen (1 MPa) at room temperature and on heating up to 600°C. During the whole experiment the nitrogen gas was forced through the sample holder at a controlled flow rate (0–10 $l_{stp.}$ min^{-1}), and then the shortest way out *via* a reducing valve and a flowmeter.

The sample temperature was measured with a W/(W, Re) thermocouple, calibrated against the melting points of Au, Pd and Pt. The plateau temperature could be kept within ± 1 K.

Two kinds of temperature programs, controlled by a PID regulator, were used in our synthesis experiments: a 'one step reaction' with one plateau temperature and a 'two step reaction' with two plateaus. The heating rate was normally 20 K min^{-1}, the cooling rate 30 K min^{-1}. Usually the gas outlet valve was opened at 1400°C on heating and closed at 1450°C on cooling.

2.3 Characterization

The surface area of the materials was measured by an independent laboratory using the BET method. The phase compositions of the reaction products were determined by X-ray powder diffraction (XRD, Guinier-Hägg-type focusing cameras) using Cu Kα_1 radiation and Si as an internal standard. The cell dimensions of the ALON phase were calculated with the PIRUM program[16] on the basis of, at most, 11 reflexions, representing *d*-values in the range 1.1–4.6 Å. The particle size was estimated by scanning electron microscopy (SEM, JEOL JSM-820, Tokyo, Japan). A few samples were subjected to elemental (N, O, C) analyses by a commercial laboratory using a fusion-gas analysis method.

In order to determine the overall composition of a product, this was ground into powder, charged in a platinum crucible and then heat treated at 1400°C for 2 h in air. Such an oxidation procedure has been reported[7] to completely transform the sample to α-Al_2O_3, expelling all nitrogen, for example according to:

$$4Al_{23}O_{27}N_5(s) + 15O_2(g) \rightarrow 46Al_2O_3(s) + 10N_2(g) \quad (2)$$

Judging from the colour of the oxidized samples, white in all cases, the residual carbon was efficiently removed by this simple procedure. This was also confirmed by chemical analysis of some samples, showing the C content to be less than 0.2 wt%. By accurate weighing of the sample before and after oxidation, the original composition, given as the AlN molar ratio $X_{AlN} = n_{AlN}/(n_{AlN} + n_{Al_2O_3})$, could be determined with an estimated accuracy better than ± 0.01, in most cases.

3 Thermodynamic Calculations

In order to interpret some of our results, we have performed thermodynamic calculations on the system Al–O–C–N by means of the computer program 'SOLGASMIX',[17] based on the principle of free energy minimization. The system was described by 35 different gas species and 8 condensed phases (Al, C, AlN, α-Al_2O_3, γ-Al_2O_3, Al_4C_3, Al_4O_4C and ALON). All $\Delta G°_f$ data were taken from the JANAF Tables[18] except those of Al_4O_4C and ALON which are from Refs 19 and 10, respectively. In all calculations ALON was regarded as a stoichiometric phase with the composition $Al_{23}O_{27}N_5$, due to the absence of data for other compositions.

Figures 2 and 3 give the calculated partial pressures of Al(g) and Al_2O(g) in equilibrium with nitrogen gas and the solid product phases after reaction between Al_2O_3 and AlN, at 2100 K and

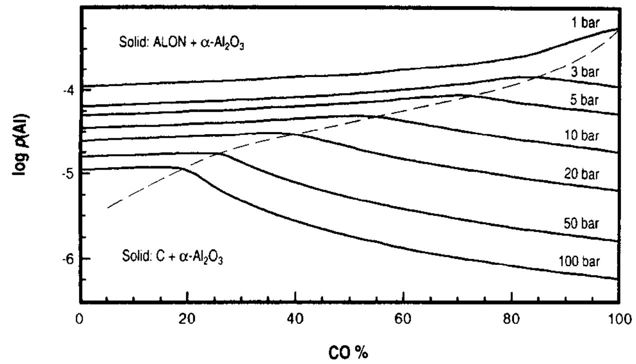

Fig. 2. Calculated equilibrium partial pressures (bar) of Al in a mixture of the products of the reaction between Al_2O_3 and AlN at 2100 K, at different pressures and CO contents in nitrogen (Al_2O_3: 9 mol, AlN: 5 mol, N_2+CO: 100 mol).

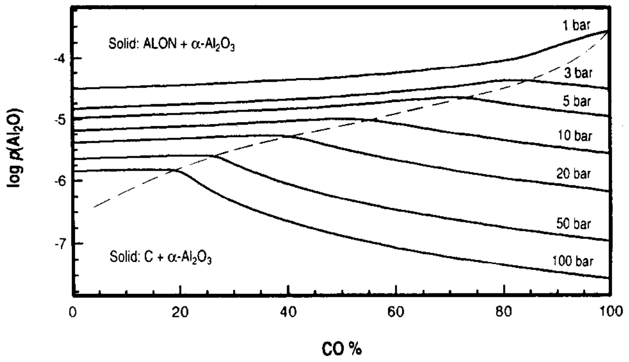

Fig. 3 Calculated equilibrium partial pressures (bar) of Al_2O in a mixture of the products of the reaction between Al_2O_3 and AlN at 2100 K, at different pressures and CO contents in nitrogen (Al_2O_3: 9 mol, AlN: 5 mol, N_2+CO: 100 mol).

different pressures and CO contents (Al_2O_3: 9 mol, AlN: 5 mol, N_2 + CO: 100 mol). The partial pressures $p(Al)$ and $p(Al_2O)$ are not sensitive to the relative amounts of starting materials. ALON ($Al_{23}O_{27}N_5$) and α-Al_2O_3 are stable products in the field above the dashed curve. Below this line, C and α-Al_2O_3 become the product phases. In the ALON formation field, $p(Al)$ and $p(Al_2O)$ increase slightly with CO content but decrease with increasing total pressure.

4 Results

4.1 Single step runs

A large number of synthesis experiments were carried out with the simple temperature program, the 'one step reaction', on the starting mixtures 'A'–'I', with Al_2O_3/C ratios between 10 and 70 (Fig. 1). Plateau temperatures and nitrogen pressures were in the ranges 1600–1860°C and 0.1—10 MPa. The results of only a selected number of runs are shown in Table 2. Also included are some 'two step reactions', as well as runs with recharged samples.

ALON appeared as a reaction product in all experiments at temperatures above 1700°C, although it turned out to be virtually impossible to prepare single phase ALON in a 'one step reaction'. The reason was that further nitridation of alumina easily occurred, yielding aluminium nitride even for a mixture with a high Al_2O_3/C ratio, such as 'G'.

Fine γ-Al_2O_3, for example in mixtures 'B' and 'D', was more reactive than coarse α-Al_2O_3, but also easily underwent substantial excess nitridation. Using the Al_2O_3–C precursor, made by the sol–gel method ('I') and expected to be highly reactive, ALON could actually be prepared at 1700°C in 3 h, but AlN formation occurred in spite of a starting composition at low X_{AlN}.

With coarse α-Al_2O_3 as in 'A', 1 h at 1750°C, 0.5 MPa was not sufficient for ALON formation in granules, which however was accomplished at 0.1 MPa. As is exemplified in Table 2, increasing the pressure hampered ALON formation for all compositions, but the difference in nitridation rate between high- and low-pressure runs was more marked with mixtures of fine-grained γ-Al_2O_3 (*cf.* runs No.5 and 6). Run No.3 with mixture 'B' demonstrates the rapid *onset* of the ALON formation reactions at T > 1800°C.

Heating at a rate of 5°C min^{-1}, instead of the normal 20°C min^{-1}, did not make much difference as to the synthesis result. A run with Ar as the furnace atmosphere during heating, and N_2 for the subsequent 1 h on the 1820°C plateau, yielded the same sample composition as an 'all nitrogen' comparison run. This suggests that the result is not very sensitive to the choice of heating rate (It is noteworthy though, that ALON failed to form in No.7, after very slow heating, 2°C min^{-1}, to 1800°C and then 1 h tempering). Neither did we find 'charge type', i.e. pellet, granule or loose powder, to be very important for the conversion rate with the starting materials used in this study.

The relative weight change (RWC), $-\Delta m/m_O$ (m_O is the charge weight), can be chosen as a general measure of conversion. However, RWC is not exclusively due to losses of CO following eqn (1), but also to extra reduction of the sample by the gas atmosphere and irreversible evaporative losses of Al-containing gas species, (e.g. aluminium or aluminium suboxides). It can be seen from Table 2 that the experimentally obtained RWC-values were always higher than the $(RWC)_{theo.}$, calculated for full conversion according to reaction (1), even for short time runs at low temperatures. The RWC ratio values given in parentheses were calculated from the analyzed AlN contents (X_{AlN}). They should be approximately equal to the experimental RWC ratios, if the weight decrease is exclusively due to reduction/nitridation of Al_2O_3 by the C reactant or the furnace atmosphere.

Table 2. The synthesis parameters and the results of the first series of nitridation runs

Run No.	*Mixture sample*	*T(°C) t (h)*	*$p(N_2)$ (MPa)*	*$\Phi(N_2)$ ($l\ min^{-1}$)*	*Sample holder*	*Product phases**	*X_{AlN} (%)*	*RWC ratio (%)***	*Comment*
1	Mix. A pellet	1800°C 1 h	5·0	5	BN	N, O	—	104	
2	Mix. B granule	1800°C 1 h	5·0	5	BN	ALON, N, O	46·6	133 (109)	
3	Mix. B pellet	1600 + 1820°C, 2 + 0 h	0·2	0·5	Mo	ALON, O, N	—	118	C granules as support charge
4	Mix. C pellet	1800°C 1 h	5·0	5	BN	N, O	33·8	104 (103)	
5	Mix. D pellet	1820°C 0.83 h	0·1	0·2	BN	ALON, N_w	51·2	152 (127)	Whiskers
6	Mix. D pellet	1820°C 0.83 h	1·0	1	BN	ALON, O_w,N_w	39·9	142 (112)	
7	Mix. E pellet	1800°C 1 h	0·5	1	BN	O, N	32·0	116 (105)	2°C min^{-1} (heating), whiskers
8	Mix. E pellet	1800°C 1 h	5·0	5	BN	O, N, $ALON_w$	—	111	
9	Mix. E pellet	1800°C 1 h	5·0	0	BN	ALON, O, N	30·9	112 (104)	Sample 8 recharged
10	Mix. E pellet	1600°C 1 h	1·0	5	BN	O, N	—	111	Whiskers
11	Mix. E pellet	1820°C 4 h	0·2 (Ar)	0	BN	ALON, N	43·0	134 (123)	Sample 10 recharged, whiskers
12	Mix. E pellet	1600+ 1820°C, 1+ 0.7h	1·0	5 + 0, 1+ 0.7h	BN	ALON, O_w,N_w	38·7	113 (119)	
13	Mix. F granule	1800°C 1 h	5·0	5	C	ALON, O, N	31·5	122 (124)	
14	Mix. F pellet	1800°C 1 h	3·0	5	BN	O, N, ALON	23·6	112 (107)	
15	Mix. F pellet	1800°C 1 h	5·0	5	BN	O, N, ALON	—	100	
16	Mix. F pellet	1800°C 1 h	5·0	0	BN	ALON, O, N	25·7	—	Sample 15 recharged

* O = Al_2O_3, N = AlN, O_w= weak XRD lines of alumina, N_w = weak XRD lines of aluminium nitride.
** RWC ratio = $(RWC)_{exp.}$/ $(RWC)_{theo}$. Figures in parentheses are RWC values based on analyzed X_{AlN}.

When a graphite sample holder was used, this material reduced the sample appreciably, even without direct contact, resulting in an extra high RWC, e.g. in run No.13. In most runs, therefore, the charge was separated from the graphite sample holder by a BN liner.

Figure 4 shows that resulting RWC versus reaction time under different conditions for compositions 'A', 'C', 'E', and 'F'. It is clear that $-\Delta m/m_O$ increases with reaction time, particularly for samples charged in the graphite holder. Increasing CO concentration in the gas to 10% caused an overall decrease of RWC, but not a lower nitridation rate (see 'special tests' below) as in the carbothermal syntheses of AlN and Si_3N_4.[13,14] No obvious dependence of conversion on gas flow rate was found. Neither was this expected, as the major effect of increasing the gas flow should be to diminish the CO concentration in the sample space. The product phase assemblage was generally ALON + AlN. In mixtures 'E' and 'F', run for short times, unreacted Al_2O_3 could also be detected.

No accurate determination of the amounts of different phases in the samples was undertaken in this study. As a rough measure of the relative contents of ALON and AlN, and in order to follow the progress of reaction, the X-ray intensity ratio $I_{ALON(400)}/I_{AlN(100)}$ was used. Figure 5 shows this ratio as a function of reaction time for pelletized starting mixtures 'A' and 'F', run in graphite sample

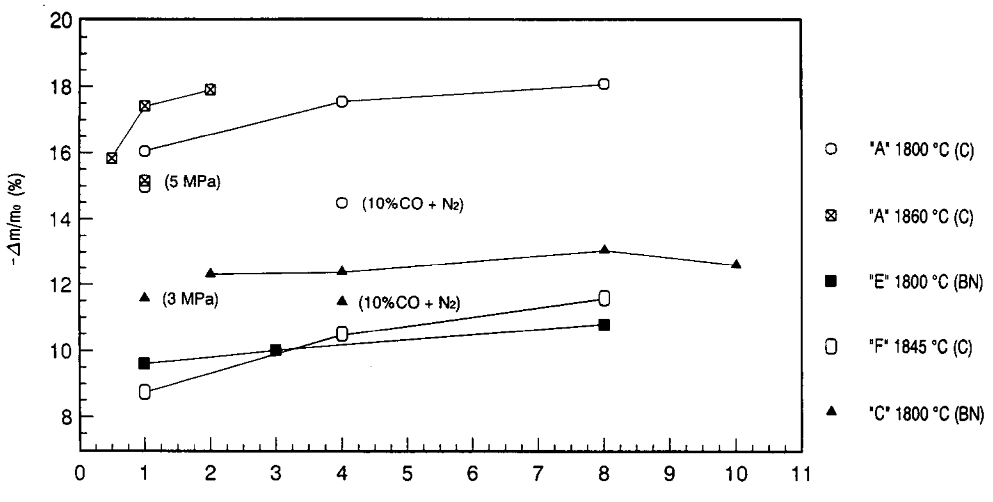

Fig. 4. RWC ($-\Delta m/m_O$) as a function of reaction time for starting mixtures A, C, E and F, run at $p(N_2) = 0.5$ MPa, $\Phi(N_2) = 5$ l min^{-1}, with different temperatures and sample holders (graphite or boron nitride). The furnace atmosphere and the pressure for some special runs are indicated in parentheses.

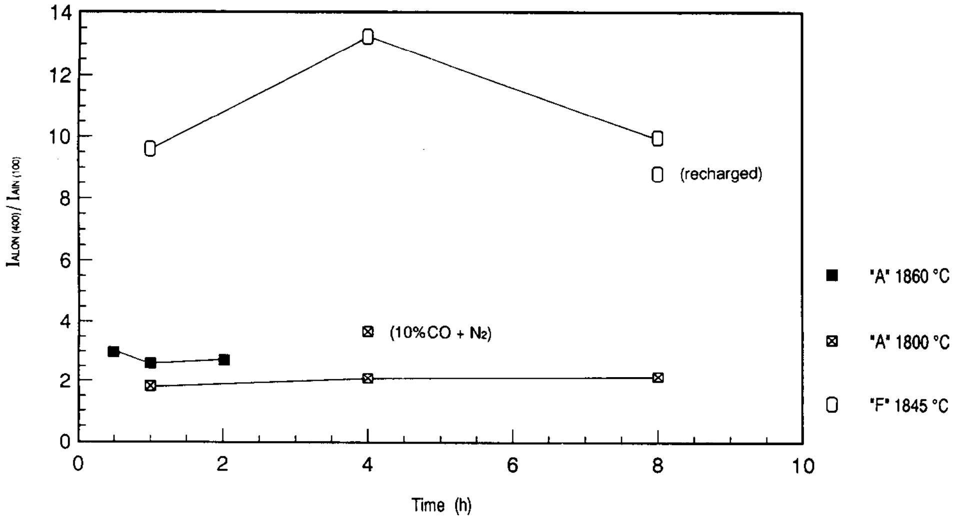

Fig. 5. The measured intensity ratio $I_{ALON(400)}/I_{AlN(100)}$ as a function of reaction time for starting mixtures A and F, run in graphite sample holders at 0.5 MPa, 5l min^{-1} and different temperatures.

holders at 0.5 MPa and different temperatures. The ratio for 'F' samples first increases with time but then decreases. Such a trend was not observed for composition 'A', possibly due to the Al_2O_3/C ratio of 'A' being much lower than that of 'F'. One sample, which had been run for 8 h, was recharged without further homogenization and the heat-treatment repeated for another 8 h, but I_{ALON}/I_{AlN} did not increase. Figure 6 shows the intensity ratio as a function of reaction time for pellets of compositions 'C' and 'E' run at 1800°C, 5 MPa, in sample holders with BN liners. For both compositions the ratio increases with time, but the rate of increase is smaller for 'C', which contains more AlN. The adverse effect on the ALON formation of an increase in pressure is evident. On the other hand, introduction of carbon monoxide into the nitrogen gas seems to slightly favour ALON formation, at the expense of AlN (Figs 5 and 6).

As stated above, none of our runs with a simple temperature programme resulted in a single-phase ALON powder. Homogenization and recharging of incompletely reacted samples and repeated heat-treatment was neither a successful means to reach this goal (compare runs No.15, and No.16 with No.14 in Table 2). Either unreacted Al_2O_3 remained, due to insufficient tempering, or AlN formed due to excessive reduction. The nitridation proceeded too far even when nitrogen was excluded during the second heat-treatment, as in runs No.10 and No.11. Nevertheless, this couple of runs, with the first annealing at only 1600°C, was an improvement upon the double run No.8 and No.9, at 1800°C. Better still was a two-step run, with a first annealing at 1600°C and a second at 1820°C without recharging, e.g. run No.12. In this case both the evaporative losses and the composition shift were smaller than in the corresponding 'single step reaction'.

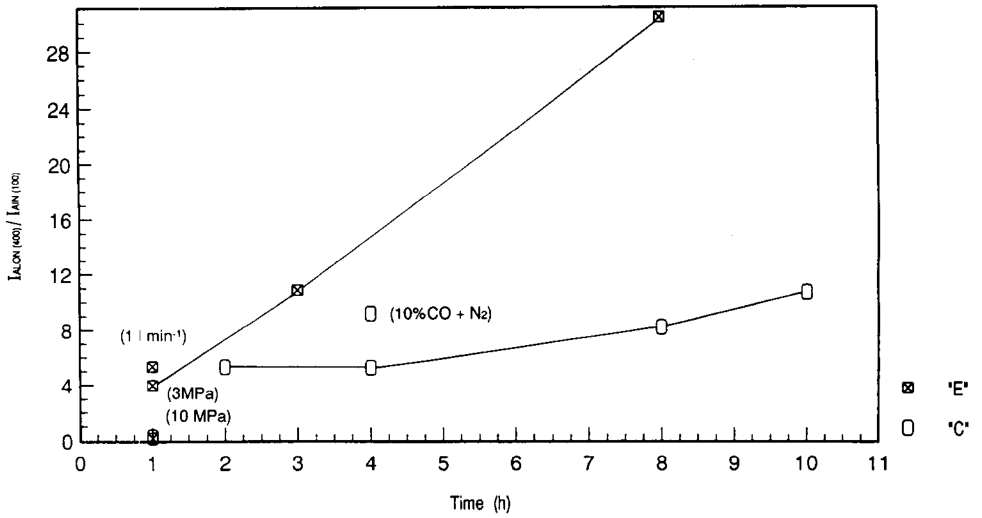

Fig. 6. The measured intensity ratio $I_{ALON(400)}/I_{AlN(100)}$ as a function of reaction time for starting mixtures C and E, run at 1800°C, 5 MPa, 5 l min^{-1} in a sample holder with BN liner. The conditions for some special runs are shown in parentheses.

4.2 Special tests

Careful control of the nitridation of Al_2O_3 thus turned out to be crucial to the carbothermal synthesis of ALON. Mainly in order to clarify the rôle of gas phase reactions in this respect, a series of special tests on pure Al_2O_3 and AlN powders were carried out. Table 3 gives the details of the experimental conditions and the results.

In all runs except No.1 and No.8, the sample was covered to prevent contamination by carbon, occasionally released from the furnace and carried away by the gas flow.

Under the experimental conditions in Nos 1–6, the Al_2O_3 charge was found to react with N_2 in the absence of C, to form substantial amounts of ALON and AlN in 4 h at 1820°C. At least qualitatively, the same results were obtained with alumina and molybdenum crucibles. Elemental analyses gave clear evidence that addition of 10% CO to the N_2 in No.6 stimulated nitridation (*cf.* No.2), while an increase in pressure had an adverse effect (No.3). Fine γ-Al_2O_3 was found to be somewhat more reactive than coarse α-Al_2O_3.

Experiment No.7, with AlN powder in a Mo

Table 3. The synthesis parameters and the results of the special tests

Run No.	*Raw material*	*Container*	*Gas*	*T (°C)* *t (h)*	*$p(N_2)$ (MPa)*	*$\Phi(N_2)$ (l min^{-1})*	*Product phases**	*ALON a_0(Å)***	*N (wt%)*
1	γ-Al_2O_3	Al_2O_3 crucible without cover	N_2	1820 4	0·2	0·6	s: N, ALON, O i: O, ALON, N	7·951 (1) 7·945(3)	—
2	γ-Al_2O_3	Mo crucible Al_2O_3 cover	N_2	1820 4	0·15	0·6	m: O, N, ALON	7·944 (2)	7.4
3	γ-Al_2O_3	Mo crucible Al_2O_3 cover	N_2	1820 4	5·0	0·6	m: O, ALON	7·948 (2)	0.8
4	γ-Al_2O_3	Mo crucible Al_2O_3 cover	N_2	1820 8	5·0	0·6	m: O, ALON	7·945 (2)	—
5	α-Al_2O_3	Mo crucible Al_2O_3 cover	N_2	1820 4	0·15	0·5	s: O, ALON, N i: O, ALON, N	7·946 (1) 7·945(2)	5.1
6	γ-Al_2O_3	Mo crucible Al_2O_3 cover	N_2+ 10% CO	1820 4	0·15	0·5	m: N, ALON, O	7·948 (2)	14.6
7	AlN		Ar	1820 4	0·15	0			—
	γ-Al_2O_3	Mo crucible and cover					i: N, ALON	7·949 (2)	
8	AlN	Mo crucible without cover	Ar	1820 4	0·15	0	m: N	—	—

* s = surface, i = interior, m= mean, N= AlN, O = Al_2O_3.
** Figures in parentheses are ± 3σ (σ ≡ the standard deviation).

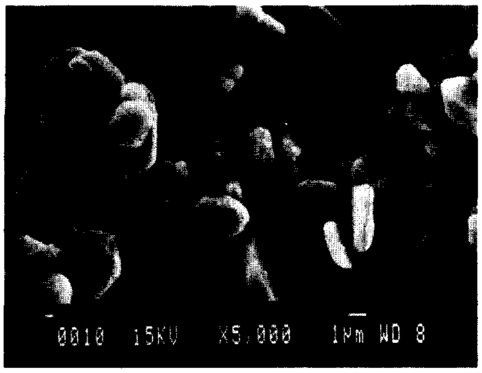

Fig. 7. SEM micrograph of the coarse α-Al_2O_3 raw material.

crucible resting on an Al_2O_3 powder bed, shows that with the reaction times and temperatures used in this series, AlN powder is affected by Al_2O_3, even at a distance of several mm, to form ALON. This reaction was mediated by gas species in the Ar atmosphere, as there was no direct contact between the two solids. Run No.8 is the 'blank' corresponding to No.7, proving that the Ar used was pure enough not to oxidize AlN.

4.3 Optimization of the ALON synthesis procedure

Based on the results of the first series of carbothermal nitridation, experimental attempts were made to optimize the synthesis parameters, aiming at monophasic powders of two different compositions within the ALON field. The 'two-step procedure' was chosen in a series of runs, with the temperature and nitrogen pressure varied, as well as the holding time at each temperature plateau. The mixtures 'B', 'C', 'D' and 'E' were selected as starting materials, either in pellet form or as loosely packed powders. The first two had the compositions $X_{AlN} = 0.39$ and 0.36; with 'B' made of fine-grained γ-Al_2O_3 and 'C' of coarse α-Al_2O_3. Mixtures 'D' with γ-Al_2O_3 and 'E' with α-Al_2O_3 had $X_{AlN} = 0.30$ and 0.29 (Fig. 1).

In order to prevent excessive reduction/nitridation, a BN compartment was used for the samples, which in most cases were contained in alumina crucibles. In some experiments the sample was also covered by Al_2O_3 powder or enclosed in an Mo capsule, embedded in a 'support charge' consisting of granules of the Al_2O_3 + C mixture in question. The effects on the synthesis result of changes in gas flow rate, heating rate and CO additions to the nitrogen gas were also studied in a few runs.

Some results of the optimization procedure are shown in Table 4. In many cases, samples for XRD were taken both from the surface and the bulk of the product pellet or powder bed. The overall composition (X_{AlN}) was determined by oxidation in air of the whole sample, as previously described.

Starting at the relatively low $X_{AlN} = 0.30$, it was possible to produce a single-phase ALON powder, both with mixtures made of fine γ-Al_2O_3 ('D') and coarse α-Al_2O_3 ('E'), and equally well with pellets and powders. Heating a 'D' pellet at 1600°C for 2 h and then at 1820°C for 40 min at atmospheric pressure in a BN environment produced a mixture of ALON + AlN and made the sample composition shift to $X_{AlN} = 0.44$. Limiting the first plateau holding time to one hour, though, was enough to retain the sample composition within the permissible limits (run No.1 in Table 4), demonstrating once more that the major reduction occurs already below ALON formation temperatures. Yet, this heat treatment was enough to yield pure ALON, although the top surface layer was found to contain small amounts of AlN as well. The large cell edge, 7.948 Å, calculated for this layer compared with the bulk, 7.945 Å, is consistent with the surface being more easily nitridized than the interior part of the pellet under the prevailing synthesis conditions. Monophasic ALON was also obtained (run No.2) using a lower heating rate from the first plateau to the second, but otherwise a temperature programme identical to that of run No.1. The effect of the slower heating was probably just to increase the annealing time. When using a higher pressure, 1.0 MPa (run No.3), a three-phase mixture was left, due to the decreased reactivity.

With the powder charge in run No.4, a longer reaction time was needed than with a pellet (run No.1). The overall composition became $X_{AlN} = 0.40$, but an excess of AlN formed in the surface parts. With Al_2O_3 powder covering the charge, the reduction/nitridation was hampered; 3.5 h heating resulted in a three-phase mixture (run No.5). In this case, the ALON cell edge was shorter in the surface layer (7.943 Å) than in the interior of the sample (7.945 Å). By the combined use of an elevated pressure (0.5 MPa), expected to reduce the nitridation rate, and a 10% CO addition to the nitrogen, a pure ALON powder was produced in run No.6 with a mean cell edge of 7.946 Å.

Optimization of the ALON synthesis based on mixture 'E' pellets typically started with runs such as No.7 and No.8, which did not yield fully reacted samples in spite of high gas flow rates and ca. 2 h tempering at 1.0 MPa. Lowering the pressure to 0.1 MPa resulted in increased nitridation ($X_{AlN} = 0.41$), although unreacted Al_2O_3 still remained (run No.9). To obtain pure ALON with a pellet charge slightly more than 2 h heat treatment was required at atmospheric pressure (run No.10).

If instead a powder of mixture 'E' was used, loosely packed in an alumina crucible, the reactivity decreased, as expected. In run No.11, heating

Table 4. The synthesis parameters and the results of runs by the 'two-step procedure'

Run No.	*Mixture sample*	*T (°C) t (h)*	*$p(N_2)$ (MPa)*	*$\Phi(N_2)$ ($l\ min^{-1}$)*	*Sample holder*	*Product phases**	*X_{AlN} (%)*	*ALON a_0(Å)***	*RWC ratio (%)****	*Comment*
1	Mix. D pellet	1500 + 1820°C, 1 + 0·7 h	0·1	0·2	BN	s: ALON, N_w i: ALON	40·4	7·948 (1) 7·945 (1)	145 (113)	
2	Mix. D pellet	1600 + 1820°C, 1 + 0·7 h	0·1	0·2	BN	s: ALON, N i: ALON	—	7·947 (1) 7·943 (1)	147	Whiskers, 2°C min^{-1} to 1820°C
3	Mix. D pellet	1400 + 1820°C, 2 + 0·7 h	1·0	0·5	BN	i: ALON, N, O	—	7·944 (1)	134	
4	Mix. D powder	1600 + 1820°C, 1 + 1·5 h	0·1	0·2	Al_2O_3	s: ALON, N_w	40·4	7·948 (1)	130 (113)	
5	Mix. D powder	1550 + 1820°C, 2 +1·5 h	0·16	1	Al_2O_3	s:ALON, O_w, N_w i: ALON, O_w, N_w	—	7·943(1) 7·945 (1)	—	Covered by Al_2O_3
6	Mix. D powder	1600 + 1820°C, 1 + 2 h	0·5	0·8 + 0, 0·5 + 2·5 h	Al_2O_3	i:ALON	—	7·946(1)	140	N_2 + 10% CO
7	Mix. E pellet	1600 + 1820°C, 1 + 0·7 h	1·0	5 + 0, 1 + 0·7 h	BN	s: ALON, O_w, N_w i: ALON, O_w, N_w	38·7	7·947 (2) 7·945 (1)	113 (119)	
8	Mix. E pellet	1400 + 1820°C, 2 + 0·7 h	1·0	0·5	BN	i: ALON, O, N_w	39·4	7·944 (1)	123 (118)	
9	Mix.E pellet	1600 + 1820°C, 1 + 0·7 h	0·1	0·2	BN	s: ALON, O_w, N_w i: ALON, O_w, N_w	41·2	7·948 (2) 7·947 (2)	121 (120)	Whiskers, 2°C min^{-1} to 1820°C
10	Mix. E pellet	1600 + 1820°C, 2 + 0·7 h	0·1	0·2	BN	s: ALON, O_w, N_w i: ALON	40·6	7·946 (1) 7·948 (1)	119 (119)	Whiskers
11	Mix. E powder	1600 + 1820°C, 1 + 2 h	0·5	0·8 + 0, 0·5+ 2·5 h	Al_2O_3	i: ALON, O, N	36·5	7·945 (1)	112 (112)	N_2+ 10% CO
12	Mix. E powder	1600 + 1850°C, 2 + 5 h	5·0	1·2	Al_2O_3	s: ALON, N i: ALON, O_w	41·1	7·948 (1) 7·948 (2)	113 (119)	
13	Mix. E powder	1600 + 1850°C, 1 + 1·5 h	0·16	1	Al_2O_3	i: ALON	39·1	7·947 (1)	115 (116)	Whiskers

* s = surface, i = interior, O = Al_2O_3, N = AlN, O_w = weak XRD lines of alumina, N_w = weak XRD lines of aluminium nitride.

** Figures in parentheses are $\pm 3\sigma$.

*** RWC ratio = $(RWC)_{exp.}/(RWC)_{theo.}$. Figures in parentheses are RWC values based on analyzed X_{AlN}.

for 3 h at 0.5 MPa was insufficient to produce a monophasic powder, in spite of CO being added to the nitrogen in order to facilitate ALON formation. At 5.0 MPa, unreacted Al_2O_3 could still be found, even after 5 h heating at 1850°C (run No.12). The overall composition had shifted to $X_{AlN} = 0.41$. In this sample, as in most of the others, the surface layer was more nitridized than the interior. This difference, however, as can be judged from the calculated ALON cell edge, seems to be somewhat less pronounced for mixture 'E' than for 'D'.

At $p(N_2) = 0.16$ MPa, pure ALON powder could be prepared after 1.5 h at 1850°C (run No.13).

All our attempts hitherto to prepare pure ALON powders from the 'B' and 'C' mixtures, with starting compositions up to $X_{AlN} = 0.40$, have been unsuccessful. Excessive reduction/nitridation, leading to ALON + AlN mixtures, could not be avoided when open sample containers were used,

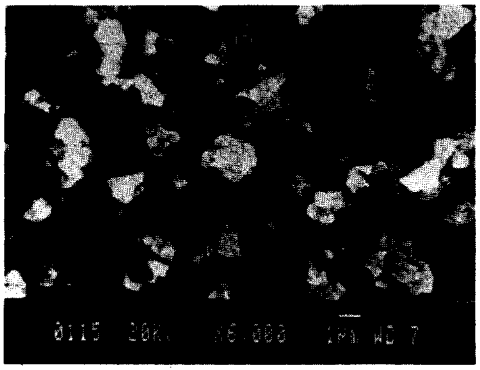

Fig. 8. SEM micrograph of the product of a two-step run with mixture E (powder) at 0.1 MPa, 0.2 l min^{-1}, 1600°C for 2 h and 1820°C for 0.67 h.

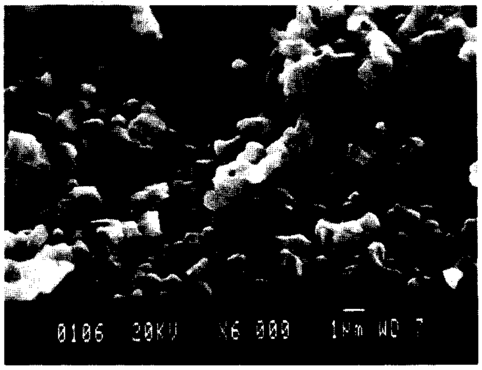

Fig. 9. SEM micrograph of the product of a one-step run with mixture D (pellet) at 1820°C for 0.83 h, 1 MPa, 1 l min^{-1}.

even in an Al_2O_3 and BN environment, and with moderate synthesis temperatures (1820°C)

By use of an elevated pressure (5 MPa), a 'support charge' or an Al_2O_3 cover, it was possible to partly control the compositional shift, also for several hours of heat-treatment at 1850°C, but even so, AlN and residual Al_2O_3 were found in the samples.

For a number of samples at the compositional limits ALON/AlN and ALON/Al_2O_3, the cell edge values of ALON, calculated with the PIRUM program, were found to be 7.938 ± 0.0001 Å (O-rich) and 7.951 ± 0.001 Å (N-rich). These were in fact the minimum and maximum cell parameters observed in the whole series of experiments, at 1750–1860°C and with cooling rates of ca. 30°C min^{-1}. Judging from Table 4 the ALON–AlN phase boundary seems to be close to X_{AlN} = 0.40 at ca. 1800°C, as determined by reoxidation of ALON samples in air.

The ALON diffraction lines on the XRD films always appeared sharp, even on close inspection of the peak profiles, excluding extended compositional variation over the samples. Yet, the cell parameter values presented in Table 4 were not sufficiently representative for the overall composition to allow a precise relationship between X_{AlN} and a_O to be established. A linear relationship between nitrogen content in ALON and cell parameter has previously been determined by Guillo.[20]

4.4 Powder morphology

Typical SEM photos (Figs 8–12) of ALON materials from this study reveal morphological differences

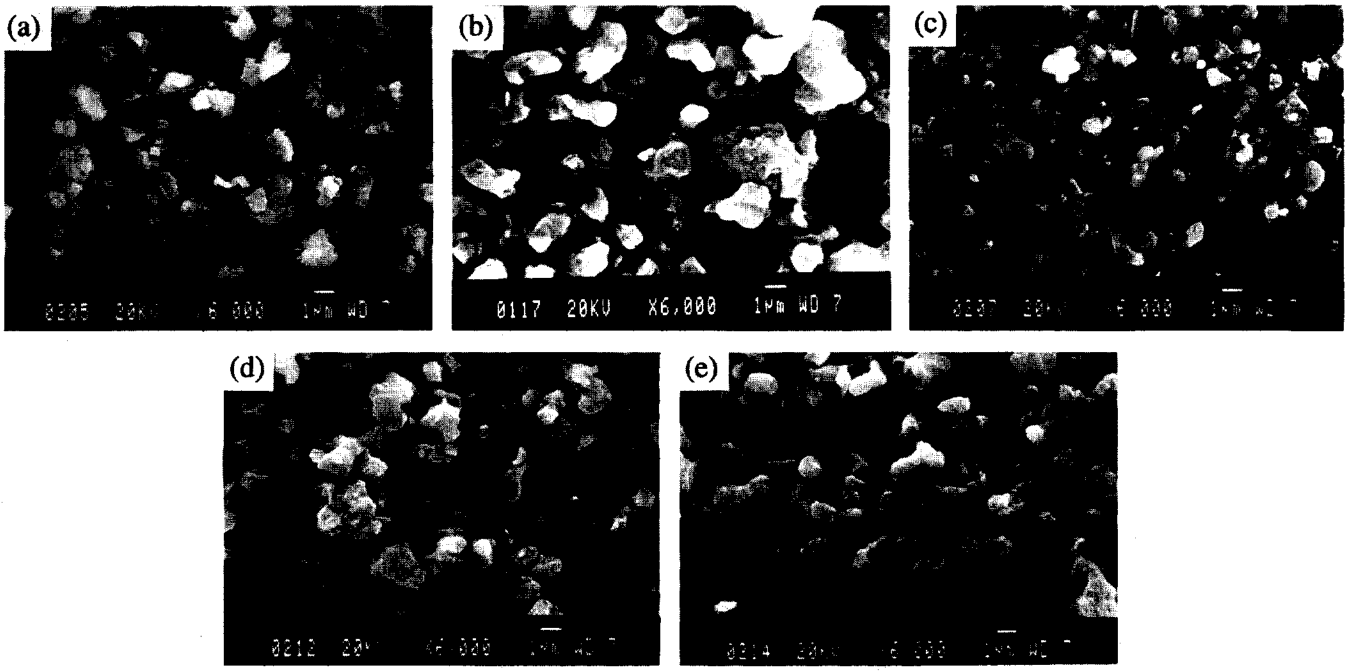

Fig. 10. SEM micrographs of the products of mixture D: (a) pellet run (two-step) at 1600°C for 2 h and 1820°C for 0.67 h, 0.1 MPa, 0.2 l min^{-1}, (b) powder run (two-step) at 1600°C for 1 h and 1820°C for 1.5 h, 0.1 MPa, 0.2 l min^{-1}, (c) powder charge covered by α-Al_2O_3 powder, run (two-step) at 1550°C for 2 h and 1820°C for 1.5 h, 0.16 MPa, 1 l min^{-1}, (d) powder run (two-step) at 1600°C for 1 h and 1830°C for 1.5 h, 5 MPa, 0.7 l min^{-1}, (e) powder run (two-step) at 1600°C for 1 h and 1820°C for 2 h in 10% CO + N_2 gas, 0.5 MPa, 0.8 l min^{-1} for 0.5 h then 0 l min^{-1}.

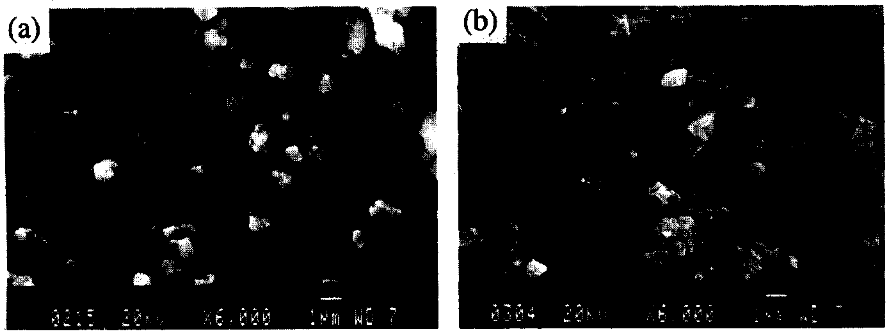

Fig. 11. SEM micrographs of the products of mixture D: (a) pellet run at 1600°C for 1 h, 1 MPa and 5 l min^{-1}, (b) product of (a) recharged and run at 1820°C for 4 h in pure N_2 gas, 0.2 MPa.

between powders prepared under different conditions.

Whether coarse or fine-grained alumina powder was the starting material made a large difference. The first type persistently yielded aggregates of irregularly shaped ALON particles, with a wide size distribution (Fig. 8), irrespective of the choice of process parameters. Yet, they proved to be finer, on an average, than the α-Al_2O_3 particles of the raw material (Fig. 7).

With fine γ-Al_2O_3 in the starting mix, the temperature programme turned out to be decisive for the ALON morphology. A 'single-step' process always resulted in densely sintered particle agglomerates (Fig. 9). On the other hand, use of a 'two-step' programme apparently was a means to reduce agglomeration, and typically to produce relatively fine-grained ALON with a moderately wide size distribution. Within this class of samples some SEM-pictures reveal small morphological differences, though, and these can be related to the different sets of process parameters used.

The slightly different features of the samples seen in Figs 10(a) and (b) suggest that the grain size is somewhat better controlled in a pellet than in a powder, loosely packed in an open crucible. However, as is shown by Fig. 10(c), a fine grain size could be achieved also with a powder bed, provided it is covered by an Al_2O_3 powder layer.

Neither the pressure, between 0.1 and 1 MPa, nor the gas flow rate and heating rate from the first to the second plateau temperature were found to be important parameters for sample morphology. On the other hand, close inspection of SEM pictures such as Figs 10(d) and (e) reveals that both application of a nitrogen pressure in excess of 2 MPa and a 10% CO-addition to the reaction gas have some influence on particle morphology; the resulting ALON particles become medium-sized, possibly with a relatively narrow distribution. Besides, the grains appear more 'crystalline', with sharp edges and corners, than other ALON powders, which are typically devoid of symmetrical features.

Figure 11(a) shows the AlN + Al_2O_3 powder that results on annealing a C + Al_2O_3 mixture at the first plateau, ultimately leading to the ALON powder in Fig. 11(b). A somewhat finer powder, similar to the starting powder in Fig. 11(a), was obtained when Ar replaced N_2 at the second plateau.

It can be seen that the products (Fig. 12(a)) obtained from fine γ-Al_2O_3 and a commercial AlN raw material are non-homogeneous and that the morphology is related to that of the starting AlN powder (Fig. 12(b)).

5 Discussion

Our experimental results exemplify some difficulties, likely to be encountered in the preparation of

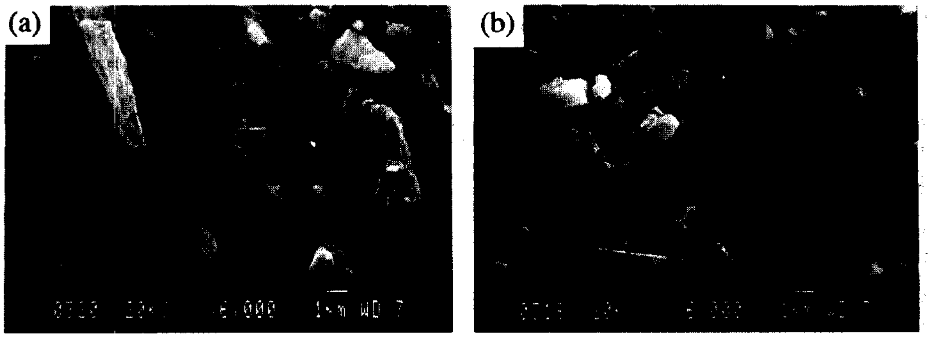

Fig. 12. SEM micrographs of (a) the product of a pellet of mixture H, run (two-step) at 1500°C for 1 h and 1820°C for 0.67 h, 0.1 MPa and 0.2 l min^{-1}, and (b) the starting AlN material.

monophasic ALON powder by the carbothermal route. However, some possible means are also presented, to circumvent the difficulties and carry out the synthesis from mixtures of carbon and alumina powders, of ordinary grade and homogenized by simple mechanical mixing. Very fine-grained reactants do not seem to be required for a successful synthesis. Use of fine powder mixtures or a sophisticated homogenization procedure, such as sol–gel, improves reactivity but will not eliminate the problem with drifting composition inherent in the high-temperature synthesis of ALON without strictly controlled O, N, C gas phase activities.[4] A common feature of carbothermal runs in a graphite furnace is namely the tendency for continuous reduction and nitridation of the sample, beyond the point determined by the carbon content of the starting mixture. As a consequence, there will also be an extra weight loss above that expected from eqn (1), and excess AlN may form.

This problem is overcome if one starts with C + Al_2O_3 mixtures with compositions corresponding to oxygen-rich ALON, thus having some tolerance for extra reduction. Such an approach was successfully used in this study and has also been the method preferred by previous workers. However, our attempted syntheses of monophasic ALON, starting with compositions near the ALON–AlN phase boundary failed, and this was due to the inability to control the reduction strictly enough. Use of a two-step heating program, an elevated pressure, CO additions to the nitrogen gas and a 'support charge' or a cover of Al_2O_3 were measures taken to achieve compositional control of the charge. All of these were effective to some degree and will be taken advantage of in future preparative work.

From a comparison of ALON cell dimensions in different parts of the samples, we conclude that application of an Al_2O_3 cover has the extra advantage of improving the charge homogeneity. Generally, a better homogeneity was obtained with coarse α-Al_2O_3 starting material than with fine γ-Al_2O_3.

When 10% CO was added to the feed gas we noted a somewhat increased intensity ratio $I_{ALON(400)}/I_{AlN(100)}$ in the products (Figs 5 and 6). This is probably a result of hampered formation of aluminium nitride,[14] as thermodynamic calculations (Figs 2 and 3) show that the formation of AlON should not be hampered by addition of CO to the N_2 gas. The increase in nitridation rate with rising CO content, found for pure Al_2O_3 powders at 1820°C (special run No.6, Table 3), is expected from thermodynamic considerations, provided gas species such as $Al_{(g)}$ and $Al_2O_{(g)}$ are somehow involved in the nitridation process. Thermodynamic calculations show that the partial pressures of these species will increase almost 100-fold when the CO content is increased from 0 to 10% in N_2 over Al_2O_3 at 2100 K.

One reason for the lower ALON formation rate at 5 MPa than at 0.1 MPa (Fig. 6 and special run No.3, Table 3) is a slower mass transport in the gas phase at the higher pressure. Furthermore, the thermodynamic calculations show that $p(Al)$ and $p(Al_2O_3)$ will decrease on raising the total pressure (Figs 2 and 3).

5.1 The two-step procedure

The improvement achieved with the 'two-step procedure', compared with the 'single-step runs', highlights the reaction chemistry below ALON formation temperatures.

From previous studies of carbothermal reduction and nitridation of Al_2O_3 at different temperatures and pressures[14] we know that in the ranges 0·1–5 MPa, 1400–1600°C the only solid compound formed is AlN. Because this phase will inevitably form prior to ALON on heating an Al_2O_3 + C mixture in N_2, ALON formation must somehow be connected with the AlN particles present, as these will remain also at 1800–1900°C. The Al_2O_3 particles in the reacting mixture are relatively stable, although partial pressures of species such as $Al_{(g)}$ and $Al_2O_{(g)}$ can be appreciable. This has been confirmed experimentally, e.g. by Lefort and Billy,[12] who established the presence of Al vapour over alumina at 1550°C in vacuum, by means of an emission spectrograph. They also observed a drastic decrease in $p(Al)$ when nitrogen was introduced in the reactor to form AlN. We therefore anticipate partial dissociation of Al_2O_3 and net losses of oxygen from the sample, particularly under the reducing conditions prevailing in a graphite furnace. These losses are expected to be higher in the surface layer of a pellet, or powder charge, than in the interior.

The gaseous aluminium is probably retained to a high degree by reaction with nitrogen, and this manifested itself in the AlN whiskers, which grew radially outward from the pellets in many of our experiments (Tables 2 and 4). (They did not grow at elevated pressure, > 1 MPa, however, which probably reflects the reduced mobility of $Al_{(g)}$ and $Al_2O_{(g)}$ following an increase in total pressure). Consequently, the surface layer of the charge will be depleted of oxygen, compared with the interior, and the resulting ALON powder will contain excess AlN near the surface. Such a segregation was observed in most of our samples, particularly in runs with high-surface area γ-Al_2O_3 at low (atmospheric) pressure, high temperature, high gas flow rate, and in a graphite sample holder. By use of a 'support charge' or an Al_2O_3 powder covering the reaction mix, this segregation could be diminished, and in some cases even an oxygen excess was left in the surface layer. Compositional variations over ALON samples, as a consequence of the gaseous environment affecting the surface parts, have been observed previously.[4]

AlN formation by the carbothermal route is not a very rapid process;[14] it is to some extent controlled by $p(CO)$, and would demand more than 1 h for a full conversion in our set-up, even at 1600°C. While the onset of ALON formation seems to be immediate, at least 0.5 h is needed for full conversion. Dissociation of 'extra' Al_2O_3 not converted to AlN by the C reagent, proceeds concurrently and may cause considerable 'over reduction' at $T > 1800°C$. We therefore conclude that the benefit of a primary annealing at low temperature, $\leq 1600°C$ in the 'two-step procedure' is that a maximum amount of AlN with respect to the C/Al_2O_3 ratio can form at temperatures low enough to cause minimum evaporative loss of oxygen. This should be a more efficient way to prepare ALON than the 'one-step procedure', implying less excessive nitridation.

The RWC values calculated from the analyzed overall compositions (X_{AlN}) in Tables 2 and 4 are rather close to the experimentally obtained values for mixtures 'F', 'C' and 'E'. Samples of mixtures 'B' and 'D', on the other hand, gave noticeably higher experimental RWCs than expected from mere reduction/nitridation of the Al_2O_3 content. Apparently these mixtures, made up of high surface area γ-Al_2O_3, were subjected to an extra weight decrease, which may be due to an irreversible loss of Al-containing gas species, such as $Al_{(g)}$ and $Al_2O_{(g)}$. If this is the case, the difference in RWC between runs No.1 and No.4 in Table 4 shows that such losses may be minimized if an Al_2O_3 crucible is used as sample container.

Part of the excess nitridation observed in most runs could be a result of a continuous decomposition of ALON with time in the graphite furnace. A dissociation process of ALON into AlN has been suggested by previous workers.[12] As a matter of fact, the compositional variation within the ALON may be described as a substitution of oxygen for nitrogen and vice versa, and hence:[10]

$$\text{ALON} + N_2(g) \rightarrow \text{AlN} + O_2(g) \quad (3)$$

The results of our special test series (Table 3), suggesting ALON to be the primary product phase with AlN subsequently appearing, seem to show that some decomposition mechanism is operating.

5.2 Particle size and morpholoy

The special tests (Table 3) tell us that in an AlN + Al_2O_3 powder mixture ALON may form, either by oxidation of the former or nitridation of the latter, without direct contact between particles. As the ALON particles bear no resemblance to the original Al_2O_3 particles, it is likely that the main direction of mass transport in the gas at ALON formation temperatures is from Al_2O_3 to AlN. In support of this view is the observation that ALON particles obtained in a two-step process from mixtures of C and fine γ-Al_2O_3 were relatively uniform, compared with powders made from coarse α-Al_2O_3 (Fig. 7). This was actually the size-dependence of process parameters previously found for AlN.[15] Consequently, mixtures of fine-grained γ-Al_2O_3 and a non-uniform, standard grade commercial AlN powder (Fig. 12(b)) produced non-uniform ALON powders (Fig. 12(a)).

The mechanism for the subsequent ALON forming reaction between the AlN matrix and the Al–O species, however, still remains to be elucidated. It should also be stressed that ALON easily forms by nitridation of Al_2O_3, even in the absence of AlN (Table 3). This may occur by the mechanism suggested in Ref. 12, and mentioned in the Introduction.

The small, yet noticeable morphological differences between powders prepared from mixtures with γ-Al_2O_3 (Figs 9–11) suggest that the rate of dissociation of Al_2O_3 is of some importance for the AlN particle size and thus the final ALON morphology. Rapid heating (single-step) led to a highly sintered powder (Fig. 9), while slow heating hampered ALON formation (run No.7 in Table 2). Possibly, the degree of supersaturation of Al or Al–O species in the gas, which is governed by the specific surface area and dissociation rate of Al_2O_3, is the crucial parameter. If so, the general tendency for particles in a pellet charge to be a little smaller than in a loose powder (*cf.* Figs 10(a) and (b)) can be understood, as well as the small grain size obtained, also with a powder charge, when an Al_2O_3 cover was used (Fig. 10(c)). This is supposed to minimize leakage of gas species from the sample, and thus to favour build-up of $p(Al)$ and $p(Al_2O)$.

A relatively large AlN particle size is expected in runs at an increased pressure and a low gas flow rate ($1\ l\ min^{-1}$),[15] and a similar trend was actually observed for ALON (Fig. 10(d)).

The relatively coarse powder obtained in a two-step run in an N_2 + 10% CO atmosphere (Fig. 10(e)) is probably due to a reduction of the Al_2O_3 surface area during the first annealing at 1600°C. For thermodynamic reasons,[14] the AlN formation rate is very low in 10% CO at this temperature, but will increase on further heating to the second plateau.

6 Conclusions

- Preparation of monophasic ALON powder by carbothermal nitridation of Al_2O_3 is complicated due to the difficulties of keeping compositional control during the process. In a graphite furnace, excess nitridation is likely to occur, mediated by Al-containing gas species generated at relatively high activities at the high synthesis temperatures required > 1600°C.
- A means to prepare pure ALON powder, without excessive reduction and AlN formation, and also to obtain a reasonably narrow particle size distribution, is to perform the synthesis in two steps; first annealing for 1 or 2 h at 1600°C, and then at 1800–1850°C for another hour. Direct heating to ALON formation temperatures, ≥ 1750°C, did not yield monophasic powders with a reasonably narrow particle size distribution.
- A high pressure in the synthesis generally lowered the nitridation rate, and may therefore be used for control of sample stoichiometry, and also particle size to some degree. To this end an Al_2O_3 sample holder with Al_2O_3 covering the charge may also be used.
- Increasing the CO content in the reaction gas (up to a certain level) has an enhancing effect on ALON formation, at the expense of AlN.
- The ALON particle morphology seems to be related to the AlN (precursor) particle morphology.
- ALON formed slowly at 1850°C in the absence of carbon, by the reaction of N_2 with a pure Al_2O_3 powder. It also formed on AlN, in the presence of Al_2O_3, without direct contact, in an Ar atmosphere.
- The crystallographic unit cell edge of the ALON samples prepared in this study at about 1800°C was found to vary between 7.938 + 0.001 Å (high-O) and 7.951 ± 0.001 Å (high-N).

Acknowledgements

We are grateful to Professor Lars Kihlborg for critical reading of the manuscript and for valuable comments. Dr Sven Westman is thanked for revision of the English text, and Mr Lars Göthe for his kind help with the X-ray diffraction. This work has been sponsored by the Swedish Natural Science Research Council (NFR).

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