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Thermodynamics of Alon II: Phase Relations

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Abstract

The dependence of the lattice parameter of γ -aluminium oxynitride (Alon) on its composition was investigated. It was found that the width of the homogeneity of Alon varies with temperature: at 1850°C Alon is the stable phase between 66 mol% Al_2O_3 (lattice parameter 0.7953 nm) and 81 mol% Al_2O_3 (lattice parameter 0.7932 nm). This region becomes smaller with lower temperatures. Below 1640 ± 10°C Alon is not stable.

Es wurde die Abhängigkeit der Gitterparameter von γ -Aluminiumoxynitrid (Alon) von der Zusammensetzung untersucht. Hierbei konnte festgestellt werden, daß die Breite des Homogenitätsbereiches von Alon mit der Temperatur variiert: bei 1850°C ist Alon im Bereich zwischen 66 Mol% Al_2O_3 (Gitterparameter: 0.7953 nm) und 81 Mol% Al_2O_3 (Gitterparameter: 0.7932 nm) stabil. Die Ausdehnung dieses Bereiches nimmt mit fallender Temperatur ab. Unterhalb 1640 ± 10°C ist Alon nicht stabil.

La dépendance des paramètres de réseau du nitrure d'oxyde d'aluminium γ (Alon) par rapport à sa composition a été étudiée. Il a été trouvé que la largeur du domaine homogène de l'Alon varie avec la température: à 1850°C l'Alon est une phase stable pour une composition variant entre 66 mol% d' Al_2O_3 (paramètre de réseau 0,7953 nm) et 81 mol% d' Al_2O_3 (paramètre de réseau 0,7932 nm). Ce domaine devient plus petit à plus basse température. En dessous de 1640 ± 10°C, l'Alon n'est plus stable.

1 Introduction

In the literature on γ -aluminium oxynitride (Alon) there seems to be some disagreement about the

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width of the stability region of this compound. Results from original research by various authors are summarized in Table 1.

As indicated in a companion paper,¹ some of the differences observed arise from the fact that Alon is stable only under a very restricted set of oxygen and nitrogen pressures and that it is not stable down to room temperature. One of the problems encountered when trying to establish the width of the homogeneity region of Alon is that the oxygen pressure under which Alon is stable is very low (about 10^{-16} bar) and this is very difficult to obtain experimentally. A second problem is that reaction rates are slow at temperatures below 1750°C and therefore it becomes difficult to obtain equilibrium.

For these reasons the furnace, the crucible and the process used influence the width of the homogeneity region found experimentally. If a furnace with graphite heating elements with a nitrogen atmosphere is used, some AlN will be made in the course of the process. In that case, it is possible that a sample initially containing too much Al_2O_3 (initial composition outside the homogeneity region) is within the homogeneity region after sintering. If a furnace is used in which no reducing agent is present, the results could be the other way around.

In this investigation, the authors have tried to establish the width of the Alon region in the pseudobinary Al_2O_3 -AlN system. Reactions were carried out in atmospheres with high and low partial oxygen pressures to study the influence of the atmosphere on the width and the position of the homogeneity region of Alon.

2 Experiments

Alon was synthesized by carbonitridation of aluminium oxide and by reacting aluminium oxide and aluminium nitride in a nitrogen atmosphere.

Table 1. Literature overview of the width of the Alon stability range

Authors	Temperature (°C)	Spinel range (mol% Al ₂ O ₃)	Reference
Lejus	1700	67–84	1
McCauley	1975	60–73	2
Guillo		68–82	3
Takebe <i>et al.</i>	1700	68–72	4
	1800	66–80	

Mixtures of Al₂O₃ (Rubis synthétique des Alpes, Jarrie, France, A15Z) with AlN (H. C. Starck, Berlin, grade C) and with carbon (Cabot, Rozenburg, The Netherlands, Elftex 125) were made in a Turbula T2C mixer (W. A. Bachofen, Basle, Switzerland). The Al₂O₃/C mixtures contained 74 w% Al₂O₃ and the Al₂O₃/AlN mixtures contained between 25 and 89 mol% Al₂O₃. At first, both types of powder were dry mixed in polyethylene flasks with nylon balls. Later the Al₂O₃/AlN powders were mixed in polyethylene flasks, using silicon nitride balls and isopropanol ('wet mixing').

The mixed powders were pressed uniaxially at 10 MPa into tablets 12 mm in diameter and 10 mm in height. These tablets were then pressed isostatically: the dry mixed Al₂O₃/AlN tablets at 100 MPa and the other tablets at 250 MPa. After pressing the surface layer of the tablets was removed by careful polishing.

X-ray diffraction (XRD) was used to measure the ratio of Al₂O₃ and AlN in the unreacted aluminium oxide/aluminium nitride tablets (using a Rigaku DMAX II/C and CuK_α radiation). For this purpose, the heights of the 104 peak of Al₂O₃ and the 002 peak of AlN (lattice spacings of 0.2552 and 0.2490 nm respectively) were determined. These peaks were chosen because they are fairly strong and close to each other (the latter minimizes the influences of the diffractometer). The peaks were

scanned near the summit, using steps of 0.01° (2θ) and a time of 50 s per step. The maximum number of counts for one step was taken to be the height of the peak.

Reactions were carried out in various furnaces (see Table 2). Sintered tablets were analysed using XRD to determine the phases present and the lattice parameter of Alon (if present). The lattice parameter was determined by plotting the lattice parameter calculated from the position of each reflection against the function $f(\theta)$, which is given by:

$$f(\theta) = \frac{\cos^2(\theta)}{\sin(\theta)} + \frac{\cos^2(\theta)}{\theta}$$

and extrapolating to $f(\theta) = 0$ (see e.g. Cullity² for the details of this procedure). Reflections in the range 70 to 125° (2θ) were used for these calculations. Diagrams were made at 4° (2θ) min⁻¹, except for some cases in which the Alon peaks were very weak and diagrams were made by step scanning with 6 s 0.01° (2θ)⁻¹.

Whenever Al₂O₃ or AlN was found in a reaction sintered sample it was used as an internal standard. For this purpose, the procedure mentioned was used to determine the lattice parameter of Al₂O₃ or AlN. Because these substances are hexagonal, use was made of the c/a ratio from the JCPDS to determine the a value. The value for the a parameter thus obtained never differed more than 10⁻⁴ nm from the value given in the JCPDS. Therefore the uncertainty of lattice parameters measured in this way is estimated to be 10⁻⁴ nm.

Al₂O₃/C and wet-mixed Al₂O₃/AlN tablets were reaction sintered in the high-frequency furnace at temperatures between 1570 and 1800°C. Al₂O₃/AlN tablets used for these experiments contained 66 mol% Al₂O₃. The sintering time for experiments in this furnace was 1 h. A graphite crucible was used without a powder bed. After sintering, the Al₂O₃/C

Table 2. Furnaces used for the experiments

Furnace	Code	Heating elements	Atmosphere
Gas-pressure	GPSF ^a	Graphite	Nitrogen (stationary) (3 and 80 bar)
Tungsten	ASF ^b	Tungsten	Nitrogen/hydrogen (88%/12%, 1 bar)
High-frequency	HFF ^c	Graphite	Nitrogen (1 bar)
Vertical tube	VTF ^d	f	Nitrogen (1 bar)
Horizontal tube	HTF ^e	f	Nitrogen (1 bar)

^a KCE Sondermaschinen GmbH, type FPW 100/150-2200-100DIL (Rödenthal, Germany).

^b Astro (Thermal Technology Inc.), type 1100V-4080-W2 (Santa Rosa, California, USA).

^c Philips, type PH 1012 (Eindhoven, The Netherlands).

^d Purpose built by Isoheat (Worksop, UK).

^e Heracus GmbH, type ROS4/50 (Hanua, Germany).

^f Elements on the *outside* of an aluminium oxide tube.

tablets were ground in an Al_2O_3 mortar and the resulting powders were analysed. The $\text{Al}_2\text{O}_3/\text{AlN}$ tablets were cut, polished on diamond discs and analysed.

In the vertical tube furnace wet-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets containing 73 mol% of Al_2O_3 were sintered in two ways. In the first case, an Al_2O_3 crucible without a powder bed, in the second a carbon crucible with a thin layer of carbon powder in it was used as a container. Both times the sintering temperature was 1750°C and the time was 3 h. The samples were cut in two and both the inside (polished) and the outside (not polished) were analysed.

Dry-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets were reaction sintered in the vertical tube furnace at temperatures between 1600 and 1750°C and times between 5 and 100 h. Wet-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets were sintered in the tungsten furnace at temperatures of 1800 (for 1 h) and 1850°C (for 1, 3 and 6 h) and in the gas pressure furnace at temperatures of 1800°C and 1850°C (for 1 h). See Fig. 1 for an overview of the compositions and temperatures used for the experiments in the vertical tube furnace, the tungsten furnace and the gas pressure furnace. In most of these experiments a powder bed consisting of Al_2O_3 , AlN and BN (75 wt% of a 73/27 mol% $\text{Al}_2\text{O}_3/\text{AlN}$ mixture and 25 w% of BN) was used to minimize the influence of the surroundings. In the vertical tube furnace a carbon crucible was used, in the tungsten and the gas pressure furnaces a boron nitride crucible was used. After sintering, the samples from the vertical tube furnace were each cut in half, polished and analysed. The samples sintered in the tungsten furnace and the gas pressure furnace had

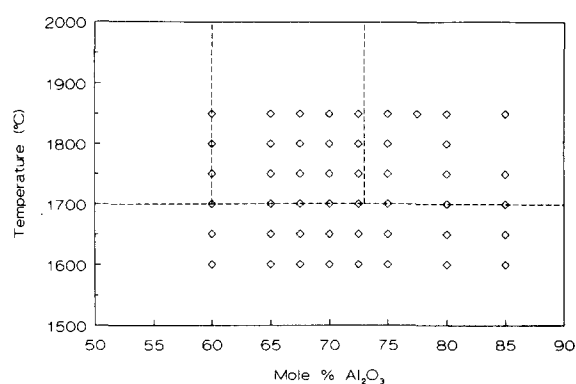


Fig. 1. Overview of the experiments in the vertical tube furnace, the tungsten furnace and the gas pressure furnace. The broken lines are from the Alon phase diagram given by McCauley & Corbin.⁹

their surface layers removed and were then polished and analysed.

Samples of single-phase Alon (synthesized at 1800°C from wet-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets with 73 mol% Al_2O_3) were annealed in the horizontal tube furnace at a temperature of 1450°C , using a glassy carbon crucible with a layer of carbon powder in it. After annealing for 100 h the surface of the samples was analysed.

The conditions for all experiments are summarized in Table 3.

3 Results

The $\text{Al}_2\text{O}_3/\text{AlN}$ ratio of the unreacted tablets can be measured with XRD with an accuracy of about 2 mol% Al_2O_3 . Dry- and wet-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets gave identical results; therefore, the wet mixing does not influence the $\text{Al}_2\text{O}_3/\text{AlN}$ ratio.

Table 3. Overview of the experiments

Starting materials	Al_2O_3 (mol%)	Mixing	Furnace code	Sintering time (h)	Sintering temperature ($^\circ\text{C}$)	Crucible	Powder bed	Atmosphere	Result
$\text{Al}_2\text{O}_3/\text{C}$	N/A	Dry	HFF	1	1 570–1 800	C	–	Flowing N_2	Table 5
$\text{Al}_2\text{O}_3/\text{AlN}$	66	Wet	HFF	1	1 630–1 650	C	–	Flowing N_2	Table 5
$\text{Al}_2\text{O}_3/\text{AlN}$	73	Wet	VTF	3	1 750	Al_2O_3	–	Flowing N_2	Table 6
$\text{Al}_2\text{O}_3/\text{AlN}$	73	Wet	VTF	3	1 750	C	–	Flowing N_2	Table 6
$\text{Al}_2\text{O}_3/\text{AlN}$	60–85	Dry	VTF	100	1 600	C	+	Flowing N_2	in text
$\text{Al}_2\text{O}_3/\text{AlN}$	60–85	Dry	VTF	40	1 650	C	+	Flowing N_2	Fig. 3(a)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–85	Dry	VTF	100	1 700	C	+	Flowing N_2	Fig. 3(a)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–85	Dry	VTF	5	1 750	C	+	Flowing N_2	Fig. 3(a)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–85	Dry	VTF	30	1 750	C	+	Flowing N_2	Fig. 3(a)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–80	Wet	ASF	1	1 800	BN	+	Flowing N_2/H_2	Fig. 3(b)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–80	Wet	ASF	1	1 850	BN	+	Flowing N_2/H_2	Fig. 3(b)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–85	Wet	ASF	3	1 850	BN	+	Flowing N_2/H_2	Fig. 3(b)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–85	Wet	ASF	6	1 850	BN	+	Flowing N_2/H_2	Fig. 3(b)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–75	Wet	GPSF	1	1 800	BN	+	N_2 (stationary) 3 bar	Fig. 3(b)
$\text{Al}_2\text{O}_3/\text{AlN}$	60–75	Wet	GPSF	1	1 850	BN	+	N_2 (stationary) 3 bar	Fig. 3(b)
Alon	(73)	N/A	HTF	100	1 450	Glassy C	–	Flowing N_2	in text

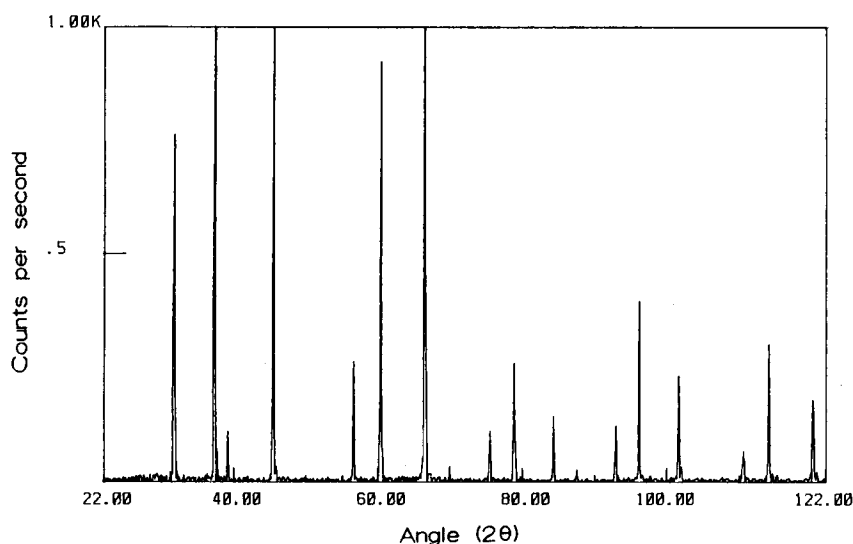


Fig. 2. Diffraction pattern of Alon (Cu- K_{α} radiation).

A typical X-ray diffraction pattern of Alon is shown in Fig. 2. As can be seen, the peaks are very sharp and allow an accurate determination of the lattice parameter. The reflections attributed to Alon are summarized in Table 4. In this table the reflections that were used to calculate the lattice parameter (provided they were found in the diagram) have a 'yes' in the last column. The reflections at

angles lower than 68° are not used, because the value derived from them is too inaccurate. The reflections at angles higher than 125° were not used for the calculations because they did not increase the accuracy.

Table 4. Reflections attributed to Alon with a lattice parameter of 0.7950 nm. The last column indicates whether the reflection was used in the calculation of the lattice parameter

H	K	L	d-value	2θ	I/I ₀	Reflection used?
1	1	1	4.5899	19.32	5	No
2	2	0	2.8107	31.81	35	No
3	1	1	2.3970	37.49	100	No
2	2	2	2.2950	39.22	6	No
4	0	0	1.9875	45.60	60	No
4	2	2	1.6228	56.67	13	No
3	3	3	1.5300	60.46	40	No
5	1	1				
4	4	0	1.4054	66.47	61	No
5	3	1	1.3438	69.95	1	Yes
6	2	0	1.2570	75.58	5	Yes
5	3	3	1.2124	78.89	10	Yes
4	4	4	1.1475	84.33	6	Yes
5	5	1	1.1132	87.56	1	Yes
7	1	1				
6	4	2	1.0624	92.94	7	Yes
7	3	1	1.0350	96.18	15	Yes
5	5	3				
8	0	0	0.9938	101.63	9	Yes
8	2	2	0.9369	110.60	2	Yes
6	6	0				
5	5	5	0.9180	114.08	14	Yes
7	5	1				
8	4	0	0.8888	120.13	7	Yes
6	6	4	0.8475	130.70	4	No
9	3	1	0.8334	135.11	12	No
8	4	4	0.8114	143.35	17	No

The results from the experiments in the high frequency furnace are summarized in Table 5. A '+' indicates that Alon was found, a '-' that it could not be found with XRD. AlN was found to form in all experiments with Al₂O₃/C tablets. The lattice parameter of Alon synthesized at 1650°C was found to be 0.7943 nm (from both Al₂O₃/C and wet-mixed Al₂O₃/AlN tablets), that of Alon synthesized at 1700°C from Al₂O₃/C tablets 0.7946 nm.

The results from the experiment with alumina and carbon crucibles in the vertical tube furnace are given in Table 6. As can be seen, the composition of the outside of the tablet reflects the stable phase under the chosen circumstances (if carbon is present, AlN is the stable phase, if alumina is used Al₂O₃ is the stable phase). At the same time the lattice

Table 5. Results from the experiments in the high frequency furnace: '+' indicates that Alon was found, '-' that it was not found. AlN was found in all experiments

Temperature (°C)	Al ₂ O ₃ /C	Al ₂ O ₃ /AlN
1570	-	
1580	-	
1590	-	
1600	-	
1625	-	
1630		-
1635	-	
1650	+	+
1700	+	
1800	-	

Table 6. Results from the sintering in the vertical tube furnace in an alumina or a carbon crucible

Crucible	Outside		Inside	
	Phases	Parameter (nm)	Phases	Parameter (nm)
Al ₂ O ₃	Alon + Al ₂ O ₃	0.7938	Alon	0.7941
Graphite	Alon + AlN	0.7942	Alon	0.7941

parameter found on the inside of the tablet does not change.

The results from the experiments in the vertical tube furnace, the tungsten and the gas pressure furnace are summarized in Fig. 3(a) and Fig. 3(b) for

temperature ranges 1650–1750°C and 1800–1850°C respectively. In the sintered tablets sometimes additional phases were present (see Fig. 3). At a temperature of 1600°C after 100h, no Alon was found. In these tablets, the ratio of Al₂O₃ and AlN was determined again (Fig. 4). On the horizontal axis the amount of aluminium oxide in the starting powder and on the vertical axis the amount determined with XRD after annealing 100h at 1600°C is indicated. The solid line indicates no change in Al₂O₃/AlN ratio. As can be seen from this figure, the tablets have become somewhat richer in Al₂O₃ during the sintering. The observed composition shifts are only slightly larger than the un-

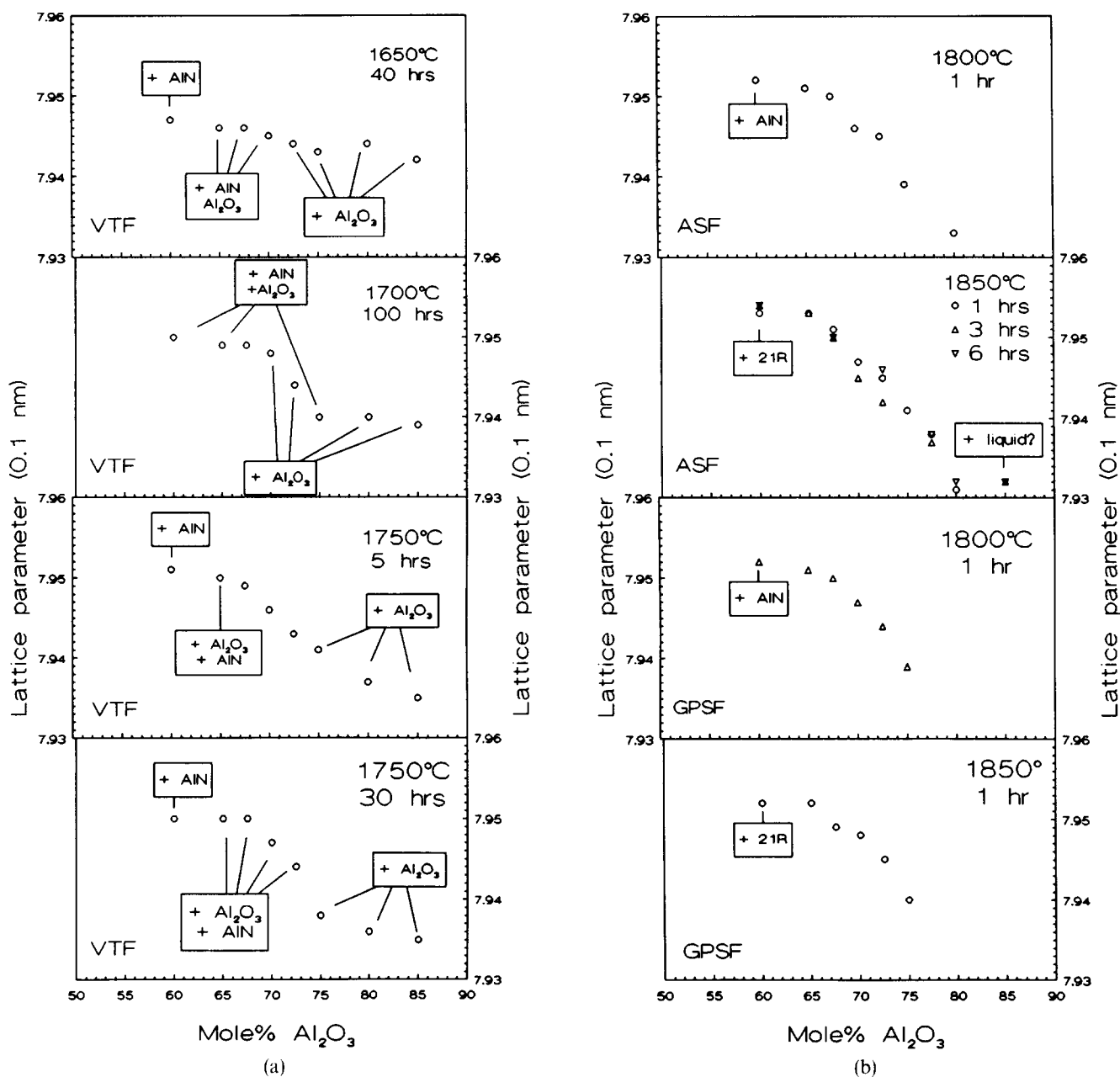


Fig. 3. Lattice parameter of Alon as a function of composition. The boxes indicate which other phases were present. The abbreviations in the lower left corner indicate the furnace used (cf. table 2). (a) Temperature region 1650–1750°C; (b) temperature region 1800–1850°C.

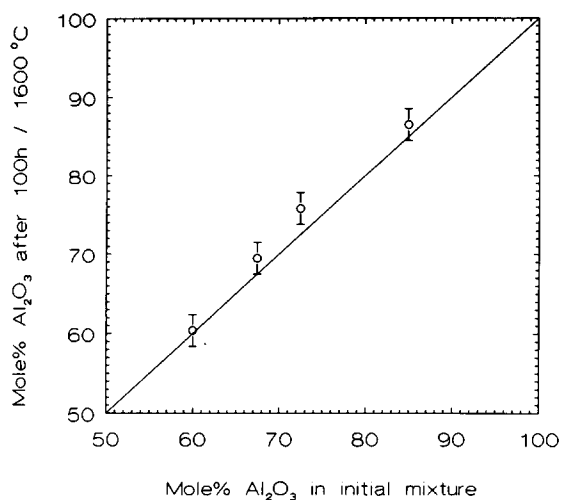


Fig. 4. $\text{Al}_2\text{O}_3/\text{AlN}$ ratio after sintering for 100 h at 1600°C . On the horizontal axis is the amount of aluminium oxide in the starting powder and on the vertical axis is the amount determined with XRD after annealing for 100 h at 1600°C is indicated. The solid line indicates no change in $\text{Al}_2\text{O}_3/\text{AlN}$ ratio.

certainly in the measurements. The surface of the Alon sample annealed for 100 h in the horizontal tube furnace was completely converted to AlN and Al_2O_3 (about 55 mol% Al_2O_3 and 45 mol% AlN).

Samples sintered in the tungsten furnace and the gas pressure furnace showed a weight loss of 1 to 2%. The samples sintered in the gas pressure furnace (wet-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets) and in the vertical tube furnace at 1750°C (dry-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets) were slightly translucent when the composition was inside the homogeneity region.

If the results obtained at different temperatures are superimposed they fall into one pattern (Fig. 5). The thick line gives the relation between the composition and the lattice parameter (at all temperatures); the other lines show the maximum

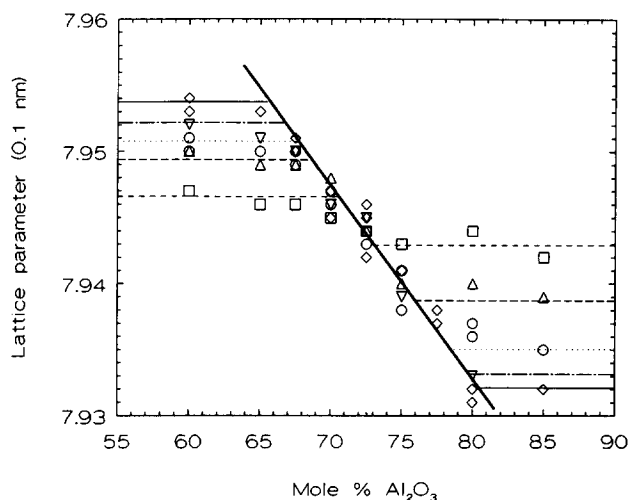


Fig. 5. Lattice parameter versus composition of Alon for various temperatures. \square , ---, 1650°C ; \triangle , ---, 1700°C ; \circ , ..., 1750°C ; ∇ , ----, 1800°C ; \diamond , —, 1850°C .

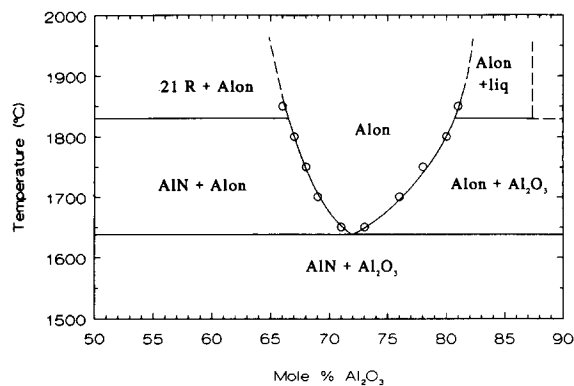


Fig. 6. The homogeneity region of Alon in the pseudobinary $\text{Al}_2\text{O}_3\text{-AlN}$ system.

and the minimum lattice parameter attainable at the indicated temperature. If the range of compositions that lead to single-phase Alon is plotted against the temperature the shape of the homogeneity region of Alon in the pseudobinary $\text{Al}_2\text{O}_3\text{-AlN}$ diagram (Fig. 6) can be found.

4 Discussion

There are a number of possible sources of error and these will be discussed in this section. The first item to discuss is the oxygen content of the AlN powder. According to the manufacturer, the AlN contained about 2.0 wt% of oxygen (an analysis of the batch used showed 1.8 wt%). From the experiments it is clear that the samples lose weight during the sintering. This could be attributed to volatilization of Al_2O (according to Corbin³ the most volatile species in his system). The oxygen content of the AlN powder and the oxygen loss by volatilization are then of the same order of magnitude. As it is not certain to which extent these reactions occur in reality, the authors choose not to take into account the oxygen content of the AlN powder nor the loss of oxygen by volatilization in the calculations regarding the composition of the samples. The maximum error made in this way is ± 0.5 mol% Al_2O_3 .

As pointed out before, Alon is not stable under the reaction conditions. Therefore the compositions will tend to 'drift away' towards the more stable phase. Because the stable phase in these experiments is sometimes AlN (when graphite is present) and sometimes Al_2O_3 (when no reducing agent is present) and the results regarding the relation between the composition and the lattice parameter are the same in both cases, it is thought that in these experiments the composition shifts due to instability are not important at temperatures higher than 1700°C . At lower temperatures the reaction times

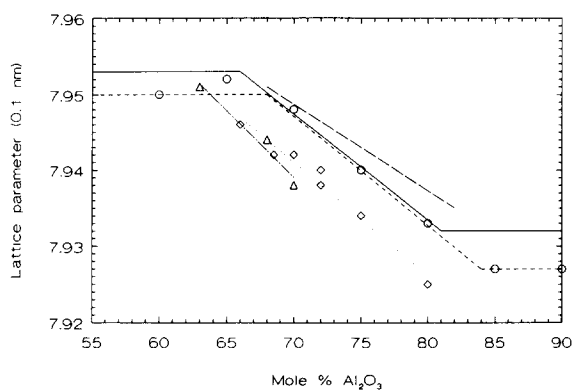


Fig. 7. Comparison of the lattice parameters from literature with the parameters found in this work. —, This investigation; ---, Lejus;¹ - · - ·, Guillo;³ · · · ·, Takebe *et al.*;⁴ - - - -, McCauley & Corbin.⁹

are so long that some influence of the surroundings is inevitable. This can be seen in the changed ratio of Al_2O_3 and AlN in the samples sintered at 1600°C in the vertical tube furnace: some Al_2O_3 is formed during the process. Therefore it seems likely that the homogeneity region of Alon is artificially shifted towards the AlN side of the phase diagram (Fig. 7) for temperatures below 1750°C . However, it is unlikely that this shift is more than a few atomic percent.

The form of the homogeneity region of Alon together with the fact that after 100 h at 1600°C no Alon is formed, while at 1650°C Alon is already formed after 1 h shows that Alon is not thermodynamically stable at the lower temperature. From Table 5 the lowest temperature at which Alon is stable is estimated to be $1640 \pm 10^\circ\text{C}$. That Alon is not found at a temperature of 1800°C is due to the fast reaction at 1800°C : all Al_2O_3 is converted into AlN after 1 h (see, for instance, Ish-Shalom⁴).

Dry-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets are not as homogeneous as wet-mixed $\text{Al}_2\text{O}_3/\text{AlN}$ tablets, due to the inferior powder processing. As a result, it is more difficult to attain equilibrium with dry-mixed tablets than with wet-mixed tablets. For that reason the experiments in the vertical tube furnace (dry-mixed tablets) show more residual Al_2O_3 and/or AlN than the experiments in the tungsten furnace and the gas pressure furnace (wet-mixed tablets).

Because Alon is not stable below 1640°C , it is possible that during the cooling down some reaction occurs backwards to Al_2O_3 and AlN . The tungsten furnace and the gas pressure furnace have cooling rates of about $20^\circ\text{C min}^{-1}$ but the cooling rate of the vertical tube furnace is only about 3°C min^{-1} . Therefore this backward reaction will be more important in the vertical tube furnace than in the tungsten furnace or the gas pressure furnace.

However, as the results from the two types of furnaces do not differ, the backward reaction, in the authors' opinion, has little or no effect on the results.

If the lattice parameters found in this work are compared with the parameters from the literature (Fig. 7), it can be seen that the present work agrees very well with the results from Lejus⁵ and reasonably with the results from Guillo.⁷ However, a few comments can be made. The temperature at which Lejus performed her experiments must have been higher than the claimed 1700°C , because otherwise the width of her Alon region would not be so large. The results of Takebe *et al.*⁸ give the same width of the region, but seem to contain some systematic error. The results from McCauley & Corbin⁹ also show a deviation. Maybe this is due to the pre-reaction step they used:³ copper at 600°C is not able to bring about the very low oxygen pressure at which AlN is stable and consequently it is possible that some of their AlN was converted to Al_2O_3 in the pre-reaction step.

5 Conclusion

The width of the homogeneity region of Alon varies with temperature: at 1850°C Alon is the stable phase between 66 mol% Al_2O_3 (lattice parameter 0.7953 nm) and 81 mol% Al_2O_3 (lattice parameter 0.7932 nm). At lower temperatures the width of the region becomes smaller. Within the homogeneity region, the relation between the $\text{Al}_2\text{O}_3/\text{AlN}$ ratio and the lattice parameter is the same for all temperatures but not all lattice parameters are attainable at all temperatures. Alon is not stable below $1640 \pm 10^\circ\text{C}$.

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