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Thermodynamics of Alon III: Stabilization of Alon with MgO

H. X. Willems, G. de With* & R. Metselaar

Centre for Technical Ceramics, Eindhoven University of Technology, POB 595, 5600 AN Eindhoven,
The Netherlands

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Abstract

The ceramic material γ-aluminium oxynitride (Alon) has been shown earlier to be thermodynamically unstable at temperatures below 1640°C. In this paper it is shown that it is possible to stabilize Alon below this temperature by addition of MgO. For this purpose, the phase diagram Al_2O_3*–AlN–MgO was investigated at 1750 and 1400°C. At 1750°C the homogeneity region of the spinel-type phase (MgAlon) extends from the* Al_2O_3*–MgO system to the* Al_2O_3*–AlN system. The lattice parameter of MgAlon can be represented by* $a = 0{\cdot}7900 + 0{\cdot}0160x + 0{\cdot}0206y$*, in which a is the lattice parameter in nm and x and y are the mol fractions of AlN and MgO respectively. At 1400°C the homogeneity region of MgAlon extends from the* Al_2O_3*–MgO system towards Alon and AlN; however, it does not reach the* Al_2O_2*–AlN system. About 25 mol% of MgO (or ~50 mol%* $MgAl_2O_4$*) has to be added to Alon to stabilize it at 1400°C. For that reason, the properties of MgAlon which is stable at 1400°C will probably be more akin to those of* $MgAl_2O_4$ *than to those of Alon.*

Der keramische Werkstoff γ-Aluminiumoxidnitrid (Alon) ist, wie in früheren Arbeiten gezeigt, unterhalb von 1640°C thermodynamisch instabil. Im folgenden soll gezeigt werden, daß es möglich ist Alon unterhalb dieser Temperatur durch Zugabe von MgO zu stabilisieren. Zu diesem Zweck wurde das Al_2O_3*–AlN–MgO-Phasendiagramm bei 1750 und 1400°C untersucht. Bei 1750°C reicht der Homogenitätsbereich der spinellartigen Phase (MgAlon) vom* Al_2O_3*–MgO-System bis zum* Al_2O_3*–AlN-System. Der Gitterparameter des MgAlons kann durch* $a = 0{\cdot}7900 + 0{\cdot}0160x + 0{\cdot}0206y$ *beschrieben werden, wobei a der Gitterparameter in nm ist und x und y die Molenbrüche von AlN beziehungsweise MgO sind. Bei 1400°C dehnt sich der Homogenitätsbereich des MgAlons vom* Al_2O_3*–MgO-System bis zum Alon und AlN aus, reicht jedoch nicht bis zum* Al_2O_3*–AlN-System. Ungefähr 25 Mol% MgO (oder ≈50 Mol%* $MgAl_2O_4$*) muß dem Alon zugegeben werden, um es bei 1400°C zu stabilisieren. Aus diesem Grund werden die Eigenschaften des bei 1400°C stabilen MgAlon wahrscheinlich mehr Ähnlichkeit mit* $MgAl_2O_4$ *haben als mit Alon.*

L'instabilité thermodynamique de l'oxynitrure d'aluminium γ (Alon) a été démontrée précédemment pour des températures inférieures à 1640°C. Dans cet article, nous montrons qu'il est possible de stabiliser l'Alon sous cette température par l'addition de MgO. A cet effet, le diagramme de phases Al_2O_3*–AlN–MgO a été étudié à 1750 et à 1400°C. A 1750°C, la région homogène de la phase spinelle (MgAlon) s'étend depuis le système* Al_2O_3*–MgO jusqu'au système* Al_2O_3*–AlN. Le paramètre de réseau, a en nm, du MgAlon peut être représenté par* $a = 0{\cdot}7900 + 0{\cdot}0160x + 0{\cdot}0206y$ *où x et y sont respectivement les fractions molaires d'AlN et de MgO. A 1400°C, la région homogène de MgAlon s'étend du système* Al_2O_3*–MgO vers l'Alon et l'AlN: cependant il n'atteint pas le système* Al_2O_3*–AlN. Il est nécessaire d'additionner environ 25% molaires de MgO (ou environ 50% molaires de* $MgAl_2O_4$*) pour stabiliser l'Alon à 1400°C. Pour cette raison, les propriétés du MgAlon stable à 1400°C seront probablement plus proches de celles de* $MgAl_2O_4$ *que de celles de l'Alon.*

1 Introduction

It has been shown previously that γ-aluminium oxynitride (Alon) is not stable below 1640°C.[1,2] As many of the foreseen applications of Alon lie in this temperature region, this instability poses serious drawbacks on the actual applicability of the

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*Also affiliated with Philips Research Laboratories, POB 80000, 5600 JA Eindhoven, the Netherlands.

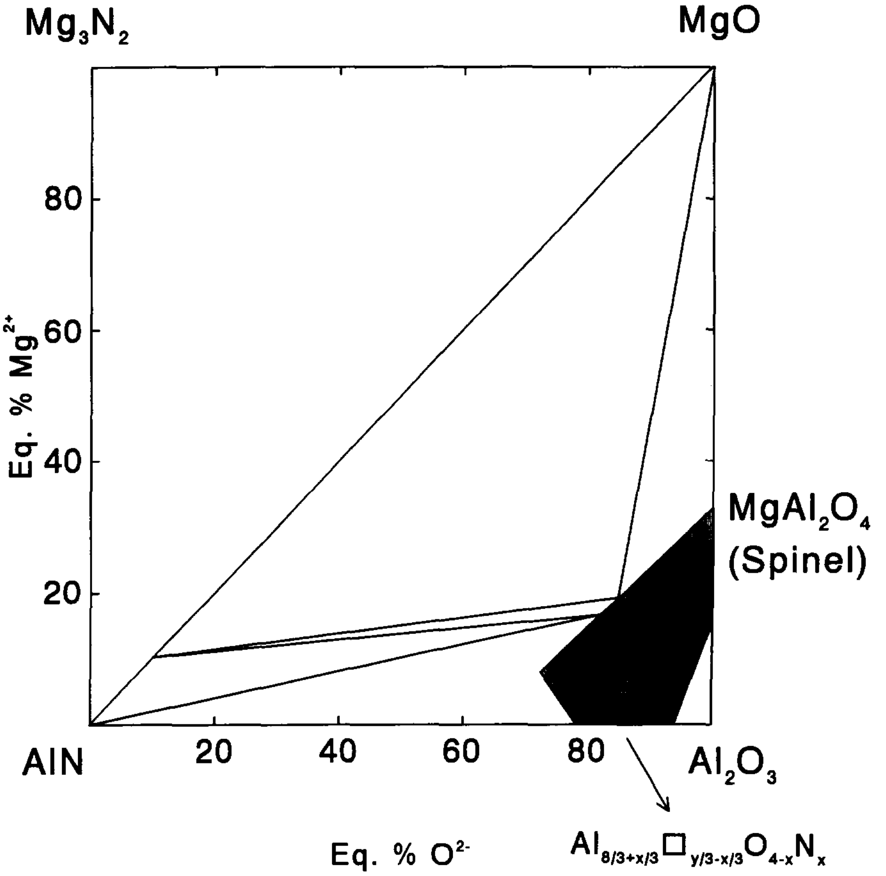

Fig. 1. Phase diagram for the Al_2O_3–AlN–MgO–Mg_3N_2 system at a temperature of 1750°C according to Weiss *et al.*[3]

material. For this reason, it would be preferable to stabilize the material at temperatures below 1640°C. In this work stabilization with MgO was considered and the Al_2O_3–AlN–MgO phase diagram was investigated. MgO was chosen as the third component because $MgAl_2O_4$ has the same crystal structure as Alon and a solid solution of MgO in Alon exists at high temperature;[3,4] furthermore, $MgAl_2O_4$ is stable down to room temperature.[5] Because $MgAl_2O_4$ can be sintered to translucency[6] and hot-pressed to transparency,[7] it is likely that the stabilized material also shows these optical properties. The solid-solution phase, which has a spinel-type crystal structure, will be denoted as MgAlon in the remaining part of this paper.

Phase diagrams from the literature are shown in Figs 1 and 2. In addition to the phases already mentioned, there is a 6AlN. MgO phase in Fig. 1 and polytype phases (27R, 16H and 21R) in Fig. 2. The Al_2O_3–AlN–MgO phase diagram was investigated at 1750°C and at 1400°C (i.e. above and below 1640°C). The first temperature was chosen slightly lower than the temperatures that were used in Ref. 4 to avoid the formation of polytypes; these extra phases are not important for the present purpose. The 6AlN . MgO phase reported in Ref. 3 was not found at 1750°C. A temperature of 1400°C was chosen because it is below 1640°C and reaction rates are not too low at that temperature.

The literature phase diagram for the Al_2O_3–MgO system is given in Fig. 3.[5] The region in which a spinel-type phase is stable is indicated by γ. In the remaining part of the paper the solid solution of Al_2O_3 and $MgAl_2O_4$ will be denoted as Spinel. At 1750°C, the Spinel region extends from 50 to 80 mol% Al_2O_3, while at 1400°C the region is much smaller (50 to 55 mol%).

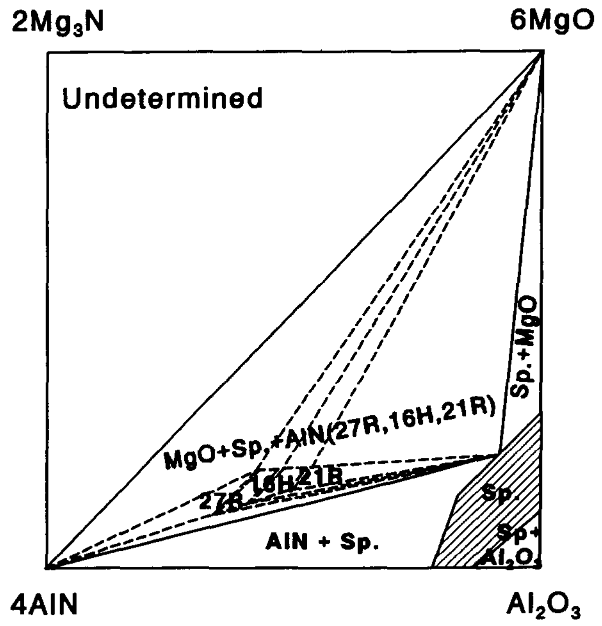

Fig. 2. Phase diagram for the Al_2O_3–AlN–MgO–Mg_3N_2 system at a temperature of 1800°C according to Sun *et al.*[4]

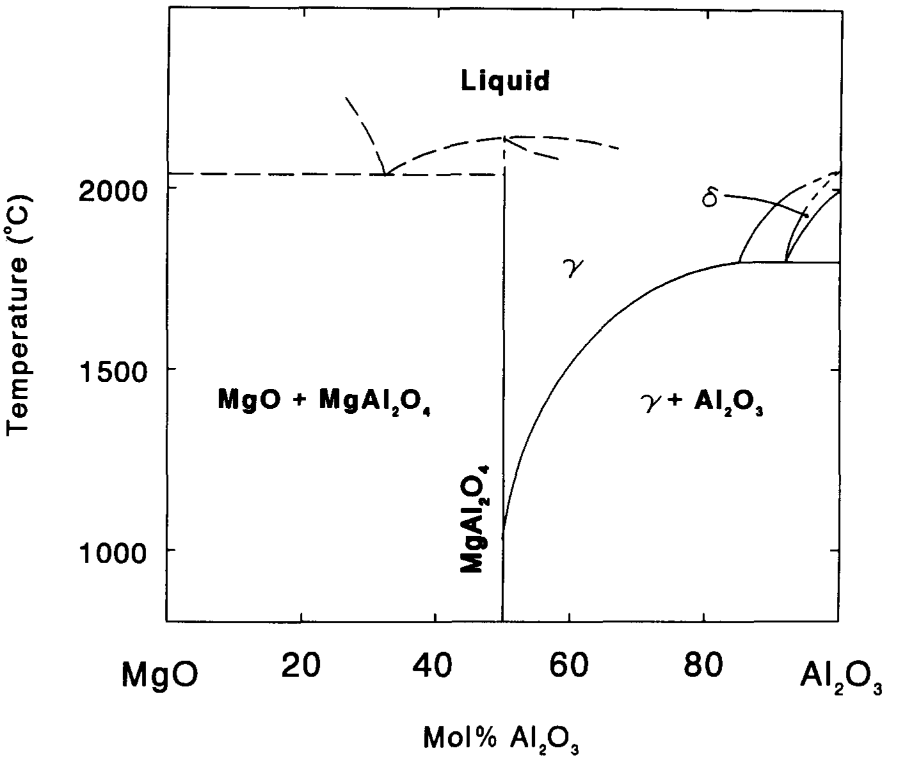

Fig. 3. Phase diagram for the Al_2O_3–MgO system.[5]

2 Experimental

Al_2O_3 (Sumitomo, Osaka, Japan, grade AKP50), AlN (H. C. Starck, Berlin, Germany, grade C) and MgO or $MgAl_2O_4$ were mixed on a roller bench with Si_3N_4 balls in isopropanol for 16 h. The codes and the compositions of the mixtures made with MgO are given in Table 1 and those of the mixtures made with $MgAl_2O_4$ in Table 2. The MgO for the WE and EDB series of powders was made by heating $MgCO_3$ (E. Merck, Darmstadt, Germany, grade 5827) for 1 h at 600°C. For the EDA series of powder mixtures MgO (E. Merck, grade 5866) was used as the Mg-containing compound. This MgO was heated for 2 h at 1000°C to remove the absorbed water. Both MgO powders were kept in vacuum exsiccators before use.

Table 1. Codes and compositions of the mixtures with MgO

Sample code	*Composition (mol fraction)*			*Sample code*	*Composition (mol fraction)*		
	Al_2O_3	*MgO*	*AlN*		Al_2O_3	*MgO*	*AlN*
WE1	0·566	0·434	0	WE27	0·402	0·299	0·299
WE3	0	0·621	0·388	WE28	0·501	0·202	0·297
WE4	0·483	0·158	0·359	WE29	0·564	0·138	0·298
WE5	0·742	0·258	0	WE30	0·645	0·056	0·299
WE6	0·365	0·110	0·520	WE31	0·638	0·150	0·212
WE7	0·025	0·074	0·901	WE32	0·652	0·248	0·100
WE8	0·615	0·235	0·150	EDA1	0·541	0·459	0
WE9	0·710	0·125	0·165	EDA2	0·730	0	0·270
WE10	0·539	0·322	0·139	EDA4	0·227	0·166	0·607
WE11	0·644	0·356	0	EDA6	0·334	0·148	0·518
WE12	0·498	0·502	0	EDA7	0·066	0·099	0·835
WE13	0	0·500	0·500	EDA8	0·331	0·610	0·059
WE14	0	0·677	0·323	EDA9	0·737	0·215	0·048
WE15	0·574	0·268	0·158	EDB1	0·568	0·432	0
WE16	0·493	0·331	0·175	EDB4	0·484	0·157	0·359
WE18	0·325	0·455	0·220	EDB5	0·743	0·257	0
WE20	0·162	0·564	0·274	EDB6	0·366	0·110	0·524
WE21	0·502	0·445	0·053	EDB8	0·616	0·234	0·150
WE22	0·496	0·391	0·113	EDB9	0·710	0·124	0·166
WE23	0·192	0·711	0·097	EDB10	0·541	0·320	0·139
WE24	0·296	0·604	0·100	EDB11	0·649	0·351	0
WE25	0·313	0·476	0·211	EDB12	0·500	0·500	0
WE26	0·320	0·355	0·325				

Table 2. Codes and compositions of the mixtures with $MgAl_2O_4$ (converted to MgO contents)

Sample code	*Composition (mol fraction)*			*Sample code*	*Composition (mol fraction)*		
	Al_2O_3	*MgO*	*AlN*		Al_2O_3	*MgO*	*AlN*
S0	0·500	0·500	0	S8	0·500	0·300	0·200
S1	0·600	0·400	0	S9	0·600	0·200	0·200
S2	0·700	0·300	0	S10	0·400	0·300	0·300
S3	0·800	0·200	0	S11	0·500	0·200	0·300
S4	0·900	0·100	0	S12	0·300	0·300	0·400
S5	0·600	0·300	0·100	S13	0·400	0·200	0·400
S6	0·800	0·100	0·100	S14	0·500	0·100	0·400
S7	0·400	0·400	0·200				

Powder batches were 20 g in weight. The weight loss of the Si_3N_4 balls during mixing was ~0·01 g per batch. After mixing, the isopropanol was removed and the powders were dried at 150°C for 24 h and passed through a 75 μm sieve. The mixed powders were pressed uniaxially at 10 MPa into tablets 12 mm in diameter and 10 mm in height. These tablets were re-pressed isostatically at 250 MPa and had their surface layers removed by careful polishing. After sintering, the weight loss was measured, the samples were examined with X-ray diffraction (XRD) and the lattice parameter (a) of MgAlon (when present) was determined.

The high-temperature experiments were done in a gas pressure furnace (KCE Sondermachinen GmbH, Rödenthal, Germany, type FPW 100/150-2200-100 DIL) at 1750°C with 3 bar of static nitrogen. Samples with MgO (from the EDA and EDB series) were sintered in a carbon crucible, while samples with $MgAl_2O_4$ (S series) were sintered in a BN crucible. When sintering powders from the EDA series, a powder bed consisting of Al_2O_3, AlN, MgO and BN (each 25 wt%) was used. Sintering time was 1 h in all cases.

The experiments at 1400°C were done in a horizontal tube furnace (Heraeus GmbH, Hanau, Germany, type R0S4/50). An overview of the conditions is given in Table 3. The powder bed mentioned in the table consisted of 60 wt% MgO, 20 wt% BN, 15 wt% AlN and 5 wt% Al_2O_3. When sintering WE powders (with MgO) in nitrogen or helium a crucible with graphite powder was positioned upstream.

In the experiments with S powders (with $MgAl_2O_4$) at 1400°C, the nitrogen flow was led through a furnace with graphite powder at 1000°C before it entered the reaction furnace. The graphite was used to keep the oxygen pressure low to prevent oxidation of AlN. The separate furnace was used to minimize the interaction between the carbon powder and the samples.

3 Results and Discussion

Weight losses were typically 1–2% for both temperatures. Compositions in the AlN–MgO system or close to that system showed much larger weight losses, typically 3–5%, but sometimes as large as 13%. This is attributed to the formation of Mg_3N_2, which is volatile under the reaction conditions. Mg_3N_2 can be formed by a reaction between AlN

Table 3. Conditions for the experiments at 1400°C

Mg compound	*Ambient*	*Crucible*	*Sample codes*	*Powder bed used*[a]	*Time (h)*
MgO	Flowing N_2	C	WE1–23	Yes	24
			WE24–32	No	24
			WE8, 10, 11, 15 WE16, 18, 21, 22	Yes	24, 48, 72
			WE1	Yes	2, 4, 8, 16, 24
			WE3	Yes	2, 4, 8, 16, 24 48, 72
			WE13	Yes	16, 24, 48, 72
	Flowing He	C	WE8, 10, 11, 15–22	Yes	24
			WE24–32	No	24
	Static air	Sillimanite	WE11	No	24, 48, 72
$MgAl_2O_4$	Flowing N_2	Glassy C	S0–S14	No	24, 48
	Static air	Al_2O_3	S0–S4	No	24, 48

[a] The powder bed, if used, consisted of 60 wt% MgO, 20 wt% BN, 15 wt% AlN and 5 wt% Al_2O_3.

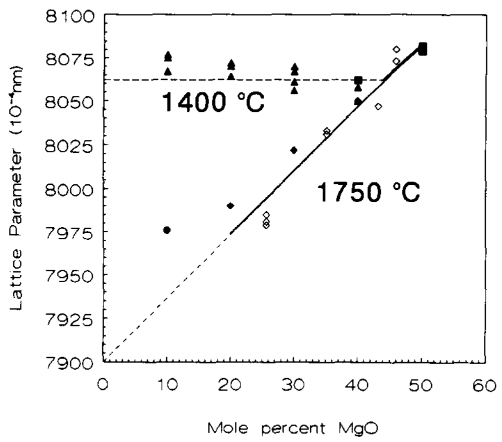

Fig. 4. Experimental results in the Al_2O_3–MgO system at 1400 and 1750°C. ◆, Spinel from mixtures with $MgAl_2O_4$ at 1750°C; ◇, spinel from mixtures with MgO at 1750°C; ●, spinel + Al_2O_3 from mixtures with $MgAl_2O_4$ at 1750°C; ■, spinel from mixtures with $MgAl_2O_4$ at 1400°C; ▲, spinel + Al_2O_3 from mixtures with $MgAl_2O_4$ at 1400°C.

and MgO or by carbothermal reduction of MgO. Problems with Mg_3N_2 volatilization were especially severe for experiments at 1400°C because, in that case, an open system was used. Some weight loss could also be due to AlN formation by carbothermal reduction of Al_2O_3 during sintering. For samples containing MgO, weight changes were sometimes positive with a maximum of 3%. No explanation except contamination could be found for these cases. However, no phases other than Al_2O_3, AlN, MgO and MgAlon were observed (with XRD) in the sintered samples.

The results of the experiments in the Al_2O_3–MgO system are summarized in Fig. 4. No significant difference in lattice parameter was observed when sintering in air or in nitrogen. The results are in agreement with the phase diagram as presented in Fig. 3.

The results of the experiments at 1750°C are summarized in Fig. 5. At this temperature, the MgAlon region extends from the Al_2O_3–AlN system to the Al_2O_3–MgO system. There are three two-phase regions: Al_2O_3–MgAlon, MgO–MgAlon and AlN–MgAlon and one three-phase region: AlN–MgO–MgAlon. No experimental results situated in the three-phase region are shown because all samples that had their starting compositions in this region showed high weight losses and consisted of AlN + MgAlon or MgO + MgAlon after sintering. It is supposed that the composition of the samples changed considerably due to the formation of Mg_3N_2.

From the preliminary experiments at 1400°C with WE1, WE3 and WE13 it was concluded that the sintering time should be 24 h or longer, because otherwise the reactions are not completed. Samples with identical compositions sintered for 24, 48 and 72 h generally contained the same phases after sintering, but the lattice parameter of MgAlon (when present) was not always the same. This is attributed to the fact that a small change in composition can cause a relatively large change in the lattice parameter.

The results from experiments at 1400°C with samples prepared with $MgAl_2O_4$ as the Mg-containing compound are presented in Fig. 6. The MgAlon region still extends to the Al_2O_3–MgO system, but not to the Al_2O_3–AlN system. Compared to the results at 1750°C there is one additional three-phase region: Al_2O_3–AlN–MgAlon. There is still a considerable solubility of Alon in $MgAl_2O_4$: Alon with a composition of about 65 mol% Al_2O_3 can be dissolved in $MgAl_2O_4$ up to approximately 50 mol%.

If all experiments done at 1400°C in nitrogen and air are plotted in one diagram, Fig. 7 is obtained. From this figure it can be seen that it is very difficult to obtain equilibrium when using MgO as a starting

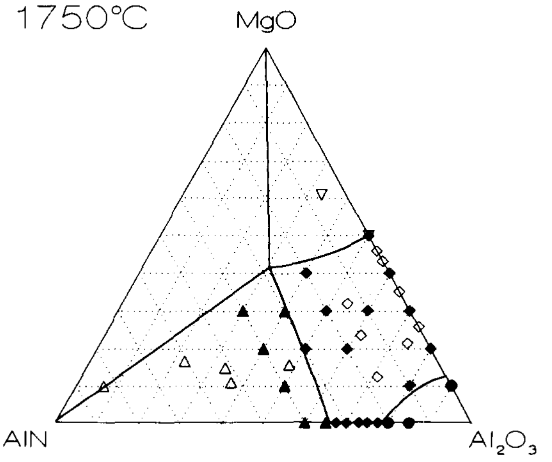

Fig. 5. Phase diagram of the Al_2O_3–AlN–MgO system at 1750°C (in mol%). ◆, ▲, ●, Experiments with $MgAl_2O_4$; ◇, △, ▽, experiments with MgO; ◆, ◇, MgAlon; ▲, △, MgAlon + AlN; ●, MgAlon + Al_2O_3; ▽, MgAlon + MgO.

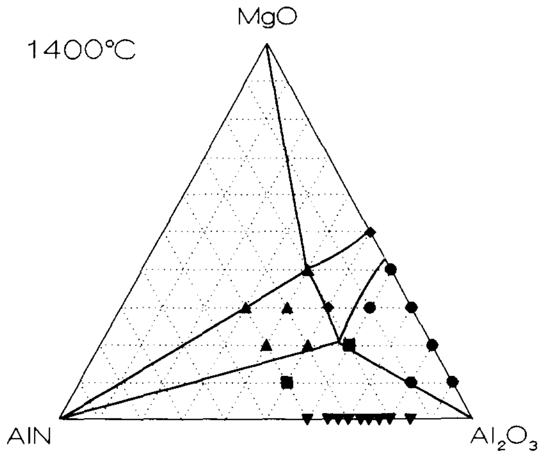

Fig. 6. Phase diagram of the Al_2O_3–AlN–MgO system at 1400°C (in mol%). The results of the experiments with $MgAl_2O_4$ are shown. ◆, MgAlon; ▲, MgAlon + AlN; ●, MgAlon + Al_2O_3; ■, MgAlon + AlN + Al_2O_3; ▼, AlN + Al_2O_3.

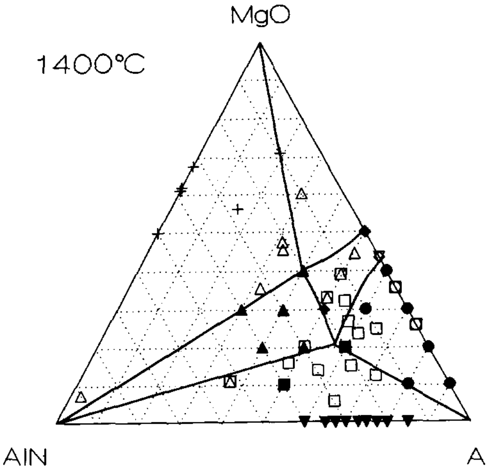

Fig. 7. Phase diagram of the Al_2O_3–AlN–MgO system of 1400°C (in mol%). ◆, ▲, ●, ■, ▼, Experiments with $MgAl_2O_4$; ◇, △, ○, ▽, □, +, experiments with MgO; ◆, ◇, MgAlon; ▲, △, MgAlon + AlN; ●, ○, MgAlon + Al_2O_3; ▽, MgAlon + MgO; ■, □, MgAlon + AlN + Al_2O_3; ▼, AlN + Al_2O_3; +, MgAlon + AlN + MgO.

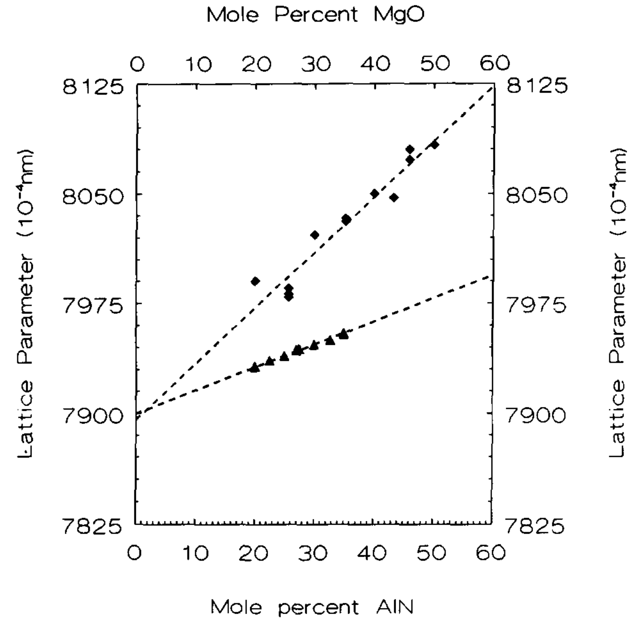

Fig. 8. Lattice parameters of Al_2O_3–AlN and Al_2O_3–MgO mixtures (with extrapolation to Al_2O_3). ◆, Lattice parameters of Spinel; ▲, lattice parameters of Alon.

material. Samples containing AlN, MgO and MgAlon after sintering are shown at their starting composition, as with the other samples. However, because weight losses were severe for these samples, the actual composition after sintering changed considerably.

A sample with a composition of approximately 50 mol% Al_2O_3, 30 mol% AlN and 20 mol% MgO, which was completely converted to MgAlon at 1840°C ($a = 0{\cdot}8018$ nm), was heat-treated at 1400°C for 100 h in the horizontal tube furnace in flowing nitrogen. The sample was contained in a carbon crucible with a thin layer of carbon powder in it. After annealing a small amount of AlN was observed with XRD, while the lattice parameter of MgAlon decreased to 0·8014 nm. This is in accordance with the results mentioned earlier, but, due to the long reaction time involved, side reactions could have some influence (e.g. a shift in composition due to carbothermal reduction or evaporation of MgO). The results from annealing experiments were therefore considered not to enhance the accuracy of the phase diagram and no more annealing experiments were performed.

Experiments in helium showed the same phases after sintering as the experiments in nitrogen. The lattice parameter of the MgAlon phase (when present) was in most cases comparable to that of the resulting phase (for the same starting composition) when sintering was performed in nitrogen. Differences were usually about 0·0005 nm but in some cases a larger difference was observed, up to 0·0050 nm. This is most probably due to a shift in composition caused by side reactions during sintering. In nitrogen carbothermal reduction of Al_2O_3 and MgO occurs, while AlN tends to dissociate when helium is used because of the low nitrogen pressure in the helium used for these experiments.

The lattice parameters of Alon from the literature[2] and the parameters of Spinel from Fig. 4 are combined in Fig. 8. The extrapolation to 0% AlN or 0% MgO intersects the y-axis at 0·7900 nm, which is exactly the lattice parameter of γ-Al_2O_3.[8] This γ-Al_2O_3 also has a spinel-type crystal structure but is not stable at this temperature. The straight lines in Fig. 8 show that Vegard's law is valid in both pseudo-binary systems. This can be interpreted as an indication that there is a single vacancy site over the whole region in both systems.

The relation between the composition and the lattice parameter can be represented as a 'plane in space' if Vegard's law is valid over the entire compositional range (see Fig. 9). The plane can be represented by the equation

$$a = 0{\cdot}7900 + 0{\cdot}0160x + 0{\cdot}0206y$$

in which a is the lattice parameter (in nm) of MgAlon

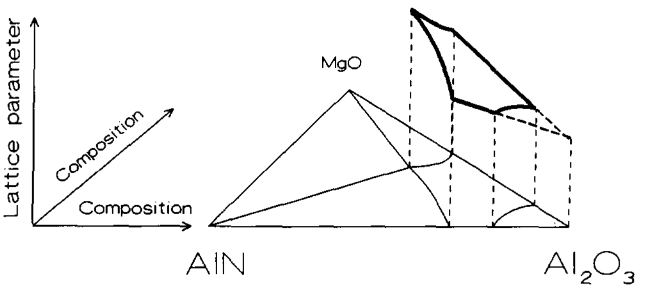

Fig. 9. Lattice parameters of MgAlon as a function of composition, constructed on the basis of Figs 8 and 5. Vegard's law is assumed to be valid over the complete compositional range.

and x and y are the mol fractions of AlN and MgO respectively. This equation was constructed from three points in the phase diagram, at which the lattice parameters were considered to be accurately known: γ-Al_2O_3 ($a = 0{\cdot}7900$ nm), $MgAl_2O_4$ ($a = 0{\cdot}8083$ nm)[8] and Alon with a composition corresponding to 72·5 mol% Al_2O_3 ($a = 0{\cdot}7944$ nm)[2]. The lattice parameters obtained at 1750°C lie approximately on this plane: the mean of the difference between the calculated and the measured lattice parameter of the 33 measurements in the MgAlon phase field was 0·0001 nm (sample standard deviation 0·0018 nm).

4 Conclusions

It has been shown that it is possible to stabilize Alon at temperatures lower than 1640°C by addition of MgO. At 1750°C the homogeneity region of MgAlon extends from the Al_2O_3–MgO system to the Al_2O_3–AlN system. The lattice parameter of MgAlon can be represented by $a = 0{\cdot}7900 + 0{\cdot}0160x + 0{\cdot}0206y$, in which a is the lattice parameter in nm and x and y are the mol fractions of AlN and MgO respectively. At 1400°C the homogeneity region of MgAlon extends from the Al_2O_3–MgO system towards Alon and AlN. However, it does not reach the Al_2O_3–AlN system. About 25 mol% of MgO (or ~50 mol% $MgAl_2O_4$) has to be added to Alon to stabilize it at 1400°C. For that reason, the properties of MgAlon that is stable at 1400°C will probably be more akin to those of $MgAl_2O_4$ than to those of Alon.

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