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Reactivity in the Al_2O_3–AlN–MgO System. The MgAlON Spinel Phase

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Abstract

The conditions for obtaining spinel aluminium and magnesium oxynitride were examined in the temperature range 1400–1850°C into the domain delimited by the spinel solid solutions: $MgAl_2O_4$–Al_2O_3 *and* AlON–Al_2O_3.

The study of some compositions having the same ratio N/Mg = 0·35 elaborated in different systems: AlN–$MgAl_2O_4$*, AlN–MgO, AlON–MgO showed the presence of intermediate spinels in which aluminium nitride or magnesium oxide are dissolved when the temperature increases, giving the MgAlON spinel. Some secondary reactions are observed under specific conditions.*

The lattice parameter evolution in regard to the composition has also been studied.

Die Bildung von Aluminiumspinell und Magnesiumoxinitrid wurde für den Temperaturbereich von 1400–1850°C und in dem Bereich der durch die Spinellmischkristalle $MgAl_2O_4$–Al_2O_3 *und* AlON–Al_2O_3 *begrenzt wird, untersucht.*

Die Untersuchung verschiedener Zusammensetzungen, die sich in unterschiedlichen Systemen, wie z. B. AlN–$MgAl_2O_4$*, AlN–MgO, AlON–MgO, mit dem selben Verhältnis von N/Mg = 0·35 bilden, ergab einen Zwischenstufenspinell, in dem sich das Aluminiumnitrid oder das Magnesiumoxid bei steigender Temperatur lösen und zur Bildung von MgAlON-Spinell führt. Unter bestimmten Bedingungen konnten verschiedene sekundäre Reaktionen beobachtet werden.*

Die Entwicklung des Gitterparameters bezüglich der Zusammensetzung wurde ebenso untersucht.

Les conditions d'obtention d'un oxynitrure d'aluminium et de magnésium de structure spinelle MgAlON dans le domaine délimité par l'existence des solutions solides spinelles $MgAl_2O_4$–Al_2O_3 *et* AlON–Al_2O_3 *ont été approfondies pour la gamme de température 1400–1850°C.*

L'étude d'une composition conservant le rapport massique N/Mg = 0·35 élaborée dans différents systèmes: AlN–$MgAl_2O_4$*, AlN–MgO, AlON–MgO a permis de mettre en évidence la présence de spinelles intermédiaires où se dissolvent en montée de température soit du nitrure d'aluminium soit de l'oxyde de magnésium pour donner lieu à la formation de MgAlON mais des réactions secondaires peuvent être présentes dans certaines conditions.*

L'évolution du paramètre de maille du spinelle MgAlON en fonction de sa composition a été également étudiée.

1 Introduction

Al_2O_3–AlN and MgO–Al_2O_3[1–3] systems have been studied for several years. For each system a crystallographic spinel solid solution exists: $Al_{8/3+x/3}\ O_{4-x}\ N_x$ (γ-AlON) and $Mg_{1-x}\ Al_{2+2x/3}\ O_4$ (on the rich limit of MgO; $MgAl_2O_4$ is a spinel). $MgAl_2O_4$ is stable down to room temperature whereas γ-AlON is metastable below 1600°C.[1–3] This instability poses serious drawbacks for the applicability of this material. Possibilities to stabilize γ-AlON phase below 1600°C have been studied[4–6] and therefore the Al_2O_3–AlN–MgO phase diagram was investigated. MgO was chosen because $MgAl_2O_4$ has the same crystal structure as γ-AlON and a solid solution of MgO in AlON has been pointed out by reaction between Al_2O_3–AlN and MgO powders at high temperature.[7–9] This solid solution which has a spinel crystallographic structure will be denoted as MgAlON. The letters in the acronym

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Table 1. Used powders

	Al_2O_3				AlN		AlON	MgO	$MgAl_2O_4$
Name	α residual	Cr 125	Cr 30	SM8	Grade C	—	—	M.30Cr	S30
Producers	Rennes University[a]	Baïkowski Chimie, France			Starck, Germany	Rennes University[b]	Rennes University[c]	Baïkowski Chimie, France	
Surface area (m^2/g)	87	105	25	8	5	30	80	25·6	30
Purity (ppm)	—	Fe 15 Na 20 Si 40 K 30 Ca 5	Fe 5 Na 12 Si 35 Ca 3 K 39	Fe 6 Na 8 Si 40 Ca 3	metallic impurities <0·1%	—	—	—	Fe 13 Na 7 Si 57 K 200 Ca 4
d_{50} (μm)	—	0·40	0·45	0·25	—	—	—	0·30	0·2
d_{90} (μm)	—	0·70	1·70	0·50	0·8	0·2	0·7	0·80	0·82
Nomenclature used	αR	γ	γ + α	α	Starck	Rennes	AlON	MgO	Sp

[a] Residual α-alumina after γ-alumina nitridation (French patents[11,12]).
[b] Nitridation of γ-alumina (French patent[11]).
[c] Nitridation of γ-alumina (French patent[12]).

are taken from the chemical elements in the solid-solution. This extent of the domain has been determined at 1750°C[8] and 1800°C,[9] it is also possible to observe it at 1350°C.[4–6] MgAlON cannot be obtained with a MgO–AlN mixture (AlN rich) at 1600°C, only the solid phase γ-AlON has been observed with volatile Mg_3N_2.[10]

The MgAlON formation mechanism proposed by Weiss *et al.* was that above 1000°C MgO and Al_2O_3 react to form $MgAl_2O_4$ in which Al_2O_3 and AlN can be dissolved at higher temperature.[8]

The present paper will precisely determine the MgAlON solid solution extent in the Al_2O_3–AlN–MgO system in the temperature range 1400–1850°C. The reactional scheme will be carried out by the study of the reactions taking place in AlN–MgO, $MgAl_2O_4$–AlN, γ-AlON–MgO and Al_2O_3–AlN–MgO systems. Then the lattice parameter evolution of this MgAlON solid solution will be investigated for different compositions.

2 Experimental Procedure

The starting materials (commercial or experimental powders) (Table 1) were mixed for 72 h by ball-milling with alumina balls in anhydrous ethyl alcohol. Long ball-milling periods may introduce some oxygen; the influence of this pick up is limited because the metallic oxides content is larger than 80%. Furthermore, the final sintered material is completely analysed in order to determine the lattice parameter variation of MgAlON solid solution. A phosphoric ester (1·5 wt%) was used as dispersant agent, slurries contained 40 wt% powders. Slurries were dried under vacuum and sieved (200 μm).

Pellets were obtained by isostatic pressing in plastic moulds at 400 MPa and were embedded in a powder for firing in a graphite furnace under nitrogen atmosphere. Some samples were prepared by hot-pressing in graphite dies at 20 MPa to simulate a closed thermodynamic system.

The studied compositions are described in Table 2.

After firing, the weight loss was measured, the bulks of the samples were examined by XRD (Cu anticathode) and the MgAlON lattice parameter (when present) was determined ($a = \pm 0{\cdot}005$ Å). An R ratio was defined for two-phased alumina–MgAlON samples equal to:

$$R = \frac{I^{\mathrm{MgAlON}}_{(400)}}{I^{\alpha\text{-}\mathrm{Al_2O_3}}_{(113)} + I^{\mathrm{MgAlON}}_{(400)}}$$

where $I(hkl)$ is the intensity of the peak diffraction for the corresponding plane of Al_2O_3 and spinel phases.

The weight variation during complete oxidation, into magnesium aluminate, gives the nitrogen content of samples (preliminarily washed with concentrated HCl to eliminate AlN and MgO). The magnesium and aluminium content were determined by atomic absorption (Service Central d'Analyse CNRS, Vernaison, France).

Table 2. Compositions used

Used nomenclature	Al_2O_3[a] (mol %)	MgO[b] (mol %)	AlN[c] (mol %)
1 Nγ	57	39	4
2 Nγ	57	21	22
3 Nγ	57	3	40
4 Nγ	75	3	22
5 Nγ	93	3	4
6 Nγ	75	21	4
7 Nγ	68	16	16
8 Nγ	66	12	22
9 Nγ	66	21	13
10 Nγ	75	12	13

[a] γ-Al_2O_3 Cr125, Baïkowski.
[b] MgO M30Cr, Baïkowski.
[c] AlN Grade C, Starck.

Table 3. Influence of powder bed on weight losses for a heat treatment at 1550°C for 1 h in a graphite furnace

Powder bed	$-\Delta m/m$ (%)
None	6–7
Al_2O_3–AlN (94 wt%–6 wt%)	6–7
Al_2O_3–AlN–Al_2O_3–BN (50 wt% (11–7–82)–50 wt%)	2–3
MgO–AlN (50 wt%–50 wt%)	1–2

3 Results and Discussion

3.1 Starting material stabilities

3.1.1 Influence of powder beds

The firing of nitrogen ceramics needs powder beds to avoid their decomposition. Several mixing powders were used, and their influence has been investigated by the weight losses of samples (Table 3). The most efficient was MgO 50 wt%–AlN 50 wt% mixing. Mg_3N_2 formed by reaction between them creates a stabilized atmosphere around the pellets and limits the decomposition.

3.1.2 'Open' and 'closed thermodynamic' systems

The graphite furnace can be considered as an 'open' system in which some reactions (Mg_3N_2 formation,[10] carbothermal reduction of Al_2O_3[13] (and MgO) can change the chosen composition of the samples. So a comparison by using a 'quasi-closed thermodynamic' system (hot uniaxial pressing in graphite dies where a limited gas phase is confined) is shown in Table 4. The results show that the same phases had been obtained in both cases, but a little difference occurs for the spinel phase lattice parameter.

3.2 MgAlON extent in Al_2O_3–AlN–MgO system

Ten compositions were studied (Table 2) in the temperature range 1400–1850°C; the heat treatments were 0·5 to 3 h. Results are shown in Figs 1 to 5. They are in good agreement with those of Willems[6] and Fievez.[4] For heat treatment at 1400°C for 3 h, two initial compositions (1 Nγ and 2 Nγ) lead to a monophased MgAlON formation. The MgAlON region extends gradually towards the AlON stability range when the temperature increases (Figs 1 to 5).

Table 4. Phases obtained at 1650°C for 0·5 h in an open or closed system (MgAlON lattice parameter is shown in parentheses)

	Open system (pressureless sintering)	Closed system (hot pressing)
2Nγ	MgAlON (8·005Å)	MgAlON (7·992Å)
4Nγ	AlN, Al_2O_3–MgAlON (7·970Å)	Al_2O_3–MgAlON (7·950Å)
6Nγ	Al_2O_3–MgAlON (8·013Å)	Al_2O_3–MgAlON (7·995Å)
8Nγ	MgAlON (7·970Å)	MgAlON (7·985Å)
9Nγ	MgAlON (7·992Å)	MgAlON (8·000Å)
10Nγ	Al_2O_3–MgAlON (7·985Å)	Al_2O_3–MgAlON (7·966Å)

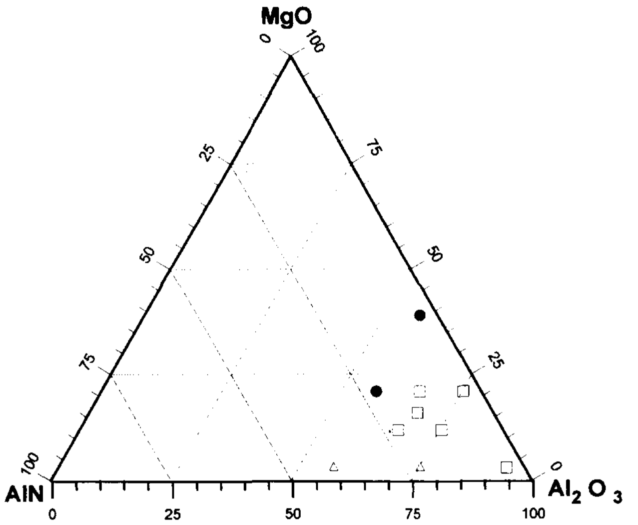

Fig. 1. Phases found after a heat treatment at 1400°C for 3 h. △, MgAlON + AlN + Al_2O_3; ●, MgAlON; □, MgAlON + Al_2O_3.

At 1850°C after 0·5 h three biphased compositions are formed:

3 Nγ represents AlN + MgAlON,
5 Nγ represents Al_2O_3 + MgAlON,
1 Nγ represents two spinel phases.

3.3 Different routes of monophased MgAlON formation

The monophased MgAlON formation has been studied in different systems: Al_2O_3–AlN–MgO, AlN–MgO, AlN–$MgAl_2O_4$ and AlON–MgO for the same ratio between the Al, Mg, O and N elements (composition 9 Nγ, Table 2). The different phases observed were studied between 1000 and 1700°C.

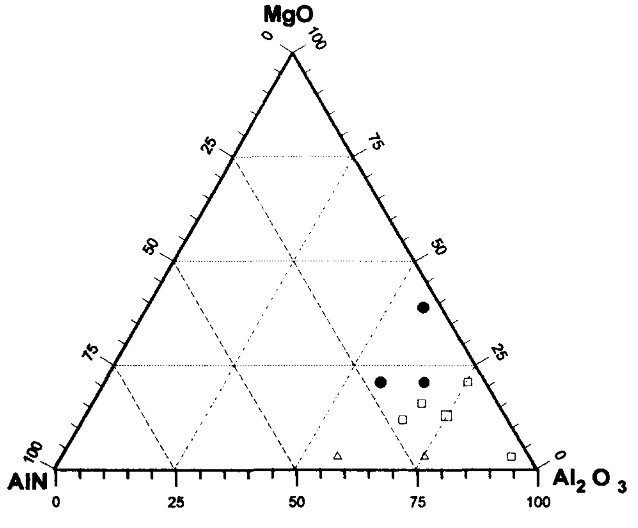

Fig. 2. Phases found after a heat treatment at 1550°C for 0·5 h. △, MgAlON + AlN + Al_2O_3; ●, MgAlON; □, MgAlON + Al_2O_3.

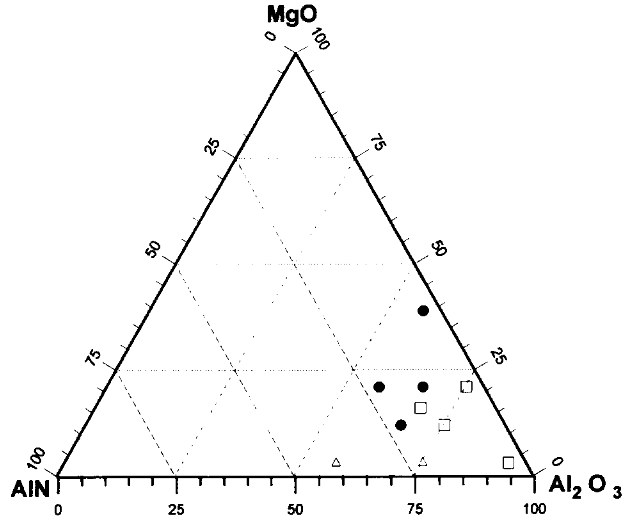

Fig. 3. Phases found after a heat treatment at 1650°C for 0·5 h. △, MgAlON + AlN + Al_2O_3; ●, MgAlON; □, MgAlON + Al_2O_3.

3.3.1 Al_2O_3–AlN–MgO system

At 1150°C all the γ-alumina has been transformed into α-alumina, MgO has disappeared in favour of a $MgAl_2O_4$ phase, and AlN is still observed. A 10-h soaking at 1150°C gives similar results: a weight loss linked to AlN disappearing was observed. Until 1350°C the same phases are observed but the content of $MgAl_2O_4$ increases while Al_2O_3 decreases. At 1400°C MgAlON and α-Al_2O_3 phases are present but after 1 h duration alumina disappears, only MgAlON is found.

The influence of different raw materials (alumina and aluminium nitride) on the kinetic reaction has been investigated at 1550°C for 1 h without a powder bed. The results are reported in Table 5.

—Best results were obtained for fine powder (codes 1 and 4)

—The reaction rate (see *R* value) does not depend on the specific surface (codes 1, 2, 3)

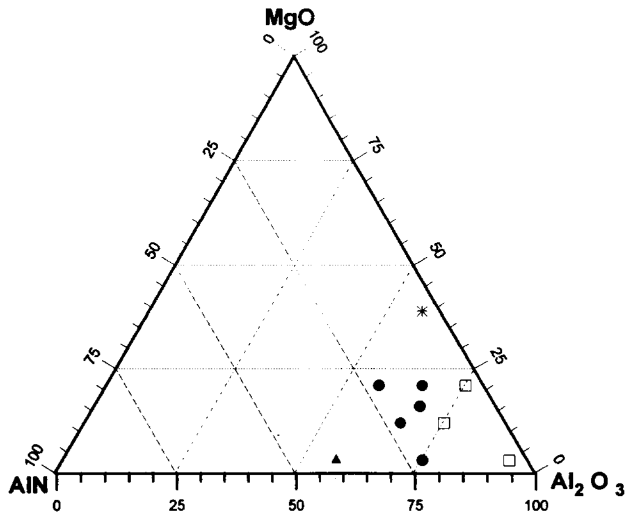

Fig. 4. Phases found after a heat treatment at 1750°C for 3 h. ▲, MgAlON + AlN; ●, MgAlON; □, MgAlON + Al_2O_3; *, two spinels.

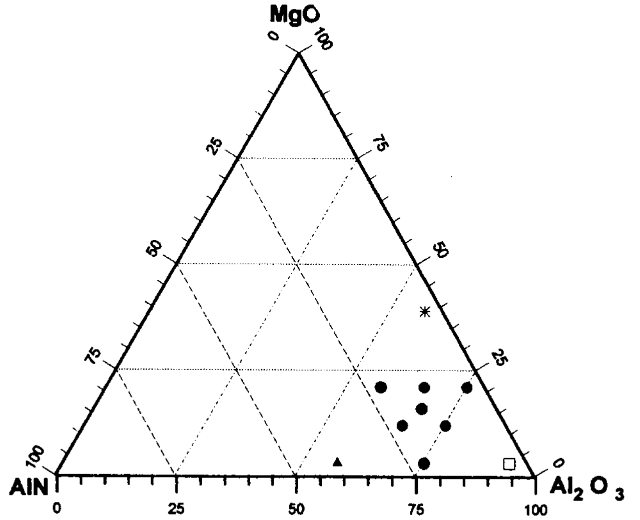

Fig. 5. Phases found after a heat treatment at 1850°C for 0·5 h. ▲ MgAlON + AlN; ●, MgAlON; □, MgAlON + Al_2O_3; *, two spinels.

—The use of γ + α-alumina induces a low reactivity even with fine AlN (codes 2 and 5).

The annealing temperature of different aluminas (SM8, Cr30, Cr125) leads to agglomerates with different hardness. These agglomerates influence the reaction rate of MgAlON formation.

3.3.2 MgO–AlN system

The chosen composition is realized by mixing 60·4 mol% MgO–39·6 mol% AlN. No reaction occurs until 1200°C. Then a severe weight loss linked to AlN disappearing was observed. At 1550°C three phases AlN, MgO (traces) and $MgAl_2O_4$ spinel were noted. No change occurs even if a fine AlN powder is used. At 1700°C for 1 h a monophased MgAlON sample was obtained, but the nitrogen content was only 3 wt%, while the initial nitrogen content was 13·3 wt%.

3.3.3 $MgAl_2O_4$–AlN system

Two non-stoichiometric spinels have been studied [$Mg_{0·980}Al_{2·013}\square_{5·6\times10^{-3}}O_4$ and $Mg_{0·870}Al_{2·086}\square_{0·043}O_4$].

Table 5. The influence of raw materials on reactvity treated for 1 h at 1550°C (without powder bed) (observed results are phases, MgAlON lattice parameter *R* values)

Code	AlN	Al_2O_3	Phases	*a* (Å)	*R*
1	Starck	γ	MgAlON	7·992	1
2	Starck	γ + α	α-Al_2O_3, MgAlON	8·025	0·54
3	Starck	α	α-Al_2O_3, MgAlON	8·010	0·69
4	Rennes	57 wt% αR, 25 wt% α	MgAlON	7·994	1
5	Rennes	68 wt% αR, 14 wt% γ + α	α-Al_2O_3, MgAlON	8·015	0·68

Table 6. Observed results at 1550°C for 1 h for different compositions with the same ratio N/Mg = 0·35

Code	AlN	$MgAl_2O_4$	Al_2O_3	a (Å) MgAlON	Phases	N (wt%) in MgAlON	R
A	Starck, 15 mol%	S30,[a] 85 mol%	—	8·06	AlN, MgAlON	1·8	—
B	Starck, 13 mol%	[b] 87 mol%	—	8·04	AlN, MgAlON	2·3	—
C	Starck, 7 mol%	S30, 40 mol%	γCr125, 53 mol%	8·02	Al_2O_3, MgAlON	(in regard to two phases) 1·62	0·68
D	Starck, 7 mol%	S30, 40 mol%	α + γCr30, 53 mol%	8·06	Al_2O_3, MgAlON	(in regard to two phases) 0·30	0·53
E	Starck, 7 mol%	S30, 40 mol%	αSM8, 53 mol%	8·01	Al_2O_3, MgAlON	(in regard to two phases) 2·8	0·49

[a] 30 m^2/g S30 Baïkowski $Mg_{0{\cdot}980}\,Al_{2{\cdot}013}\,\square_{5{\cdot}6\times10^{-3}}\,O_4$ (□, cationic vacancy).
[b] No nomenclature of Baïkowski (Al/Mg = 1·25).

Until 1200°C no reaction occurs; at 1700°C samples were monophased in both cases and the lattice parameter was the same (a = 7·994 ± 0·005 Å). A difference was observed at 1550°C: two phases were present (AlN + MgAlON), but a higher nitrogen concentration was allowed by a higher cationic vacancies concentration in the initial spinel phase (for □ = 0·043, [N] = 2·3 wt%; □ = 5·6 × 10^{-3}, [N] = 1·8 wt%) (Table 6, codes A and B). From 1200 to 1550°C a severe weight loss was observed.

The influence of alumina dissolution in $MgAl_2O_4$ to enhance the MgAlON formation was studied for different alumina powders (γ, γ + α, α) (Table 6, codes C, D, E) at 1550°C for 1 h. Fine alumina powder (γ) was the most efficient in leading to much more MgAlON, but the oxynitride phase is richer in nitrogen for α-alumina. Fine powders enhance a secondary reaction to give Mg_3N_2 (nitrogen loss).

3.3.4 γ-AlON–MgO system

Two γ-AlON powders with respectively 2·7 and 4 wt% N [a = 7·940 and 7·950 Å] were prepared by γ-Al_2O_3 nitridation according to the patent in Ref. 12. These spinel powders were heat treated at 1700°C (stabilization of the phase[1]) then mixed with MgO (atomic ratio N/Mg = 0·35).

These samples, treated for 1 h at 1550°C, contain α-Al_2O_3 (small amount) and MgAlON phases. A 10-h soaking at 1550°C or 1 h at 1700°C induces MgAlON only (Table 7). For all these experiments, no weight variation was observed and the nitrogen content in the oxynitride phase was equal to the initial concentration.

Table 7. Lattice parameter evolution for AlON–MgO composition treated at 1550°C

	Starting mixture	Treatment 1 h at 1550°C	Treatment 10 h at 1550°C
Phases and spinel lattice parameter (Å)	AlON + MgO, 7·940	MgAlON + α-Al_2O_3, 8·016	MgAlON, 7·999

3.4 Lattice parameter evolution of MgAlON solid solution

Starting from the basic formula of γ-Al_2O_3, $Al_{8/3}\,\square_{1/3}\,O_4$, with a lattice parameter of 7·900 Å, γ-AlON and $MgAl_2O_4$ solid solutions can be described by dissolution of AlN and MgO respectively in γ-Al_2O_3.[4,6] The lattice parameter evolution of each solid solution is:

$$a\gamma\text{-AlON} = 7{\cdot}900 + 0{\cdot}150[\text{AlN}]\text{Å} \quad (1)$$

$$a\text{MgAl}_2\text{O}_4 = 7{\cdot}900 + 0{\cdot}375[\text{MgO}]\text{Å} \quad (2)$$

with [AlN] and [MgO] in mol% of each component.

In the space (lattice parameter a(Å), [AlN], [MgO]) these lines determine a plane which has the following equation:

$$a = 7{\cdot}900 + 0{\cdot}375[\text{MgO}] + 0{\cdot}150[\text{AlN}]\text{Å} \quad (3)$$

This equation describes well the lattice parameter of MgAlON solid solution, as shown in Table 8. In contradiction with the model of Weiss *et al.*[8]

Table 8. Comparison of experimental and calculated lattice parameters for different compositions

Formulation	Experimental value, a (Å)	Calculated value, a (Å)
$Mg_{0{\cdot}376}\,Al_{2{\cdot}54}\,\square_{0{\cdot}084}\,O_{3{\cdot}628}\,N_{0{\cdot}372}$	7·992	8·007
$Mg_{0{\cdot}200}\,Al_{2{\cdot}71}\,\square_{0{\cdot}090}\,O_{3{\cdot}469}\,N_{0{\cdot}530}$	7·985	7·985
$Mg_{0{\cdot}360}\,Al_{2{\cdot}478}\,\square_{0{\cdot}162}\,O_{3{\cdot}846}\,N_{0{\cdot}154}$	7·992	7·994
$Mg_{0{\cdot}386}\,Al_{2{\cdot}522}\,\square_{0{\cdot}092}\,O_{3{\cdot}662}\,N_{0{\cdot}338}$	7·997	8·008
$Mg_{0{\cdot}415}\,Al_{2{\cdot}579}\,\square_{0{\cdot}005}\,O_{3{\cdot}432}\,N_{0{\cdot}568}$	8·016	8·020
$Mg_{0{\cdot}769}\,Al_{2{\cdot}219}\,\square_{0{\cdot}012}\,O_{3{\cdot}805}\,N_{0{\cdot}195}$	8·065	8·061
$Mg_{0{\cdot}438}\,Al_{2{\cdot}492}\,\square_{0{\cdot}070}\,O_{3{\cdot}649}\,N_{0{\cdot}351}$	8·009	8·017
$Mg_{0{\cdot}649}\,Al_{2{\cdot}313}\,\square_{0{\cdot}038}\,O_{3{\cdot}763}\,N_{0{\cdot}236}$	8·051	8·045

□, Cationic vacancy.

which predicts only one combination between Mg and N (nitrogen content determines the lattice parameter), the present model gives more influence to Mg than to N with regard to the value of the lattice parameter of the MgAlON phase.

4 Reactional Scheme

It is clear that no kinetics studies are possible in such a system where intermediates occur during chemical reactions, therefore a degree of reaction cannot be defined.

Aluminium nitride is not stable in contact with oxide powders such as MgO, $MgAl_2O_4$ or Al_2O_3. In the temperature range 1200–1400°C it reacts with MgO and $MgAl_2O_4$ to form volatile Mg_3N_2, so weight losses are observed. To avoid (or limit) this phenomenon a powder bed made of 50 wt% MgO–50 wt% AlN must be used in an 'open' system. Above 1350°C AlN reacts with MgO or $MgAl_2O_4$ to give an oxynitride spinel phase by an intermediate solid solution $Mg_{1-x}Al_{2+2x/3}O_4$. The nitridation is most efficient if this intermediate phase has much more cationic vacancies which can be created by Al_2O_3 dissolution. The nitrogen diffusion in the oxide spinel phase allows a loss of nitrogen in an open thermodynamic system.

If nitrogen is present in an initial spinel phase (γ-AlON), magnesium diffuses into the spinel crystallographic cell, and the anionic redistribution does not lead to nitrogen loss.

It is difficult to correlate the lattice parameter of spinel phase with the concentration of either Mg or N, although it seems that Mg is predominant to impose the lattice parameter value with regard to N (Table 8), as indicated by the coefficients of [MgO] and [AlN] in eqn (3). The cation Mg^{2+} is larger than Al^{3+}, the polarization of the bonding is lower, so the interatomic distance is increasing.

5 Conclusion

In the Al, Mg, O, N system the MgAlON formation always derives from an intermediate spinel solid solution, either magnesium aluminate or aluminium oxynitride spinel. If nitrogen is not fixed in an initial spinel structure there is a weight loss by volatile Mg_3N_2 formation. When magnesium aluminate is used as magnesium source it is efficient in dissolving some alumina to create some cationic vacancies which increase the reaction rate of MgAlON formation.

The lattice parameter evolution of the MgAlON solid solution is described by a plane. This plane was defined by the lattice evolution of the spinels $MgAl_2O_4$ and γ-AlON. The preponderant influence is due to the MgO content.

A recent work from Willems *et al.* is in agreement with these results.[14]

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