

MgAl₂O₄– γ -Al₂O₃ solid solution interaction: mathematical framework and phase separation of α -Al₂O₃ at high temperature

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Abstract. Although existence of MgAl₂O₄– γ -Al₂O₃ solid solution has been reported in the past, the detailed interactions have not been explored completely. For the first time, we report here a mathematical framework for the detailed solid solution interactions of γ -Al₂O₃ in MgAl₂O₄ (spinel). To investigate the solid solubility of γ -Al₂O₃ in MgAl₂O₄, Mg–Al spinel (MgO– n Al₂O₃; $n = 1, 1.5, 3, 4.5$ and an arbitrary high value 30) precursors have been heat treated at 1000°C. Presence of only non-stoichiometric MgAl₂O₄ phase up to $n = 4.5$ at 1000°C indicates that alumina (as γ -Al₂O₃) present beyond stoichiometry gets completely accommodated in MgAl₂O₄ in the form of solid solution. $\gamma \rightarrow \alpha$ alumina phase transformation and its subsequent separation from MgAl₂O₄ has been observed in the Mg–Al spinel powders ($n > 1$) when the 1000°C heat treated materials are calcined at 1200°C. In the mathematical framework, unit cell of MgAl₂O₄ (Mg₈Al₁₆O₃₂) has been considered for the solid solution interactions (substitution of Mg²⁺ ions by Al³⁺ ions) with γ -Al₂O₃. It is suggested that combination of unit cells of MgAl₂O₄ takes part in the interactions when $n > 5$ (MgO– n Al₂O₃).

Keywords. MgAl₂O₄ spinel; Al₂O₃; solid solution; phase transformation; X-ray diffraction.

1. Introduction

To achieve phase pure MgAl₂O₄ (spinel) composition, the primary criteria is to develop a process that would produce precursor powder having Mg²⁺:Al³⁺ ionic ratio exactly as 1:2. In the last few decades, there has been dramatic development of process technologies yielding new materials having diverse material properties of different functional behaviours. Structurally, MgAl₂O₄ is a unique ceramic material with multipurpose applications (Shimizu *et al* 1985; Cynn *et al* 1992; Urita *et al* 1993; Ganesh *et al* 2002; Ji-Guang *et al* 2000) from bulk high temperature refractory use to high value critical applications such as humidity sensors, optical devices for visible and infrared transmission, protective armors, fusion reactor powder core insulating material, etc. Unit cell of MgAl₂O₄ spinel is cubic and has 8 formula units of MgAl₂O₄ with 64 tetrahedral and 32 octahedral sites. All 8 Mg²⁺ ions occupy tetrahedral sites and the 16 Al³⁺ ions are present in octahedral sites. Generally Mg–Al spinels are represented as MgO– n Al₂O₃: for $n = 1$ it is stoichio-

metric and any other value of n results in non-stoichiometric spinels.

Synthesis of MgAl₂O₄– γ -Al₂O₃ solid solution phases for $n > 1$ (MgO– n Al₂O₃) has been reported in literature (Suwa *et al* 1986; Shou-Yong *et al* 2000; Zawrah 2004). Shou-Yong *et al* (2000) and Zawrah (2004) reported MgAl₂O₄– γ -Al₂O₃ solid solution phase in the powder material at 1080°C and 1000°C respectively. Suwa *et al* (1986) showed similar solid solution phase in the temperature range 500–1025°C, when they heat treated gels with a ratio of 93 wt% Al₂O₃ to 7 wt% MgO. They also revealed phase separation of α -Al₂O₃ from the solid solution at 1100°C and achieved 100% separation at this temperature in presence of 0.5 wt% α -Al₂O₃ seeds.

In the present investigation, room temperature coprecipitation technique has been applied to prepare precursors evolving Mg–Al spinel powders having $n \geq 1$. Powders have been heat treated at 1000°C and 1200°C for 3 h to evaluate MgAl₂O₄ formation, MgAl₂O₄– γ -Al₂O₃ solid solution interaction and precipitation of α -Al₂O₃ from MgAl₂O₄. A detailed mathematical framework of MgAl₂O₄– γ -Al₂O₃ solid solution has been built to verify the interactions.

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2. Experimental

Analytical grade magnesium and aluminium nitrates have been used to prepare a mixed solution containing $Mg^{2+}:Al^{3+}$ ionic ratio as 1:2. Ammonia solution was added to precipitate the mixed hydroxides having $MgO-nAl_2O_3$ molar ratio as $n = 1, 1.5, 3, 4.5$ and an arbitrary high value 30. Precipitation was controlled by changing the pH to evolve such molar ratios in the calcined products. The products were designated as A1, A2, A3, A4 and A5 for $n = 1, 1.5, 3, 4.5$ and 30 respectively. Each precipitate was thoroughly washed with de-ionized water to free it from NO_3^- and NH_4^+ ions. Then it was filtered under vacuum and dried at $110^\circ C$ for 48 h. The dried powders were calcined at 1000° and $1200^\circ C$ for 3 h, ground in an agate mortar and sieved through B.S. 200 mesh for XRD analysis.

Diffractometer with CuK_α radiation (PW 3050/60 Goniometer, PANalytical, Netherlands) was used for both qualitative and quantitative XRD studies of the different calcined powders. From d_{hkl} values, unit cell parameters of Mg–Al spinels were measured. For quantification of $MgAl_2O_4$ and $\alpha-Al_2O_3$ phases in the powders calcined at $1200^\circ C$, Rietveld analysis was used.

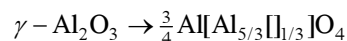
3. Results and discussion

3.1 $1000^\circ C$ XRD interpretation

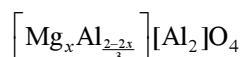
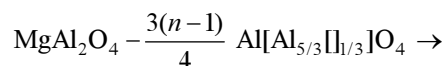
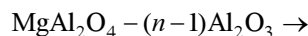
X-ray spectra of $1000^\circ C$, 3 h calcined powders (figure 1) show that each curve contains only $MgAl_2O_4/MgAl_2O_4-\gamma-Al_2O_3$ solid solution phase except for A5, where both $MgAl_2O_4-\gamma-Al_2O_3$ solid solution and $\gamma-Al_2O_3$ phases are present. Shift of Bragg's angle of different crystal planes of $MgAl_2O_4$ with increasing amount of alumina addition suggests that $\gamma-Al_2O_3$ goes into solid solution in $MgAl_2O_4$. Work of Shou-Yong *et al* (2000) also reveals that alumina in the form of $\gamma-Al_2O_3$ forms complete solution with $MgAl_2O_4$ when $n = 5$ and it was assumed that the same effect would continue even with higher n . In the present investigation, a maximum arbitrary value $n = 30$ has been considered to evaluate whether small amount of spinel (<5 wt%) can accommodate high amount of $\gamma-Al_2O_3$. There is close similarity in XRD patterns of A2, A3, A4 with A1, but A5 differs a lot from others. Hence it can be suggested that $MgAl_2O_4$ can accommodate a certain amount of $\gamma-Al_2O_3$.

For most prominent $MgAl_2O_4$ peak at [113] plane, table 1 shows variation of Bragg's angle, d_{113} and unit cell parameter a given by $a = \sqrt{h^2 + k^2 + l^2} \times d_{hkl}$ of Mg–Al spinels ($1000^\circ C$, 3 h) for different n . Increase in Bragg's angle with increasing values of n clearly indicates decrease in unit cell parameter of Mg–Al spinels. Replacement of Mg^{2+} ions (larger ionic radius) by Al^{3+} ions (smaller ionic radius) suggests reduction of unit cell

parameter. $MgAl_2O_4-\gamma-Al_2O_3$ solid solution interaction can be represented as



and



where

$$x = \frac{4}{3n+1}.$$

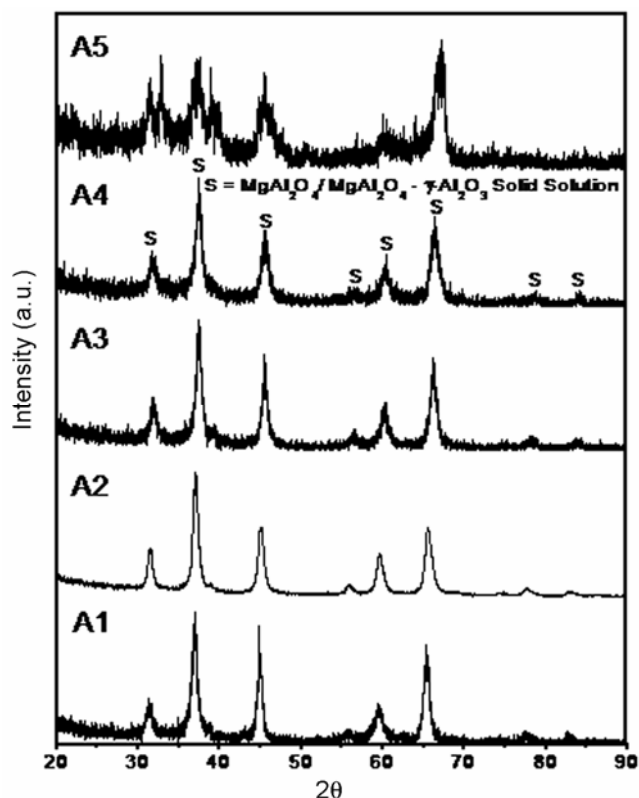
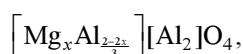


Figure 1. XRD spectra of Mg–Al spinels for $n \geq 1$ ($MgO-nAl_2O_3$) at $1000^\circ C$, 3 h.

Table 1. Variation of Bragg's angle, interplanar spacing and unit cell parameter of Mg–Al spinels for different n ($MgO-nAl_2O_3$) at $1000^\circ C$, 3 h.

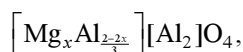
	$n = 1.0$	$n = 1.5$	$n = 3.0$	$n = 4.5$
$2\theta (^\circ)$	36.94	37.02	37.40	37.65
d_{113} (nm)	0.2434	0.2428	0.2404	0.2401
a (nm)	0.8072	0.8053	0.7974	0.7964

Here x has been determined from the equivalence of the relations MgO- n Al₂O₃ and

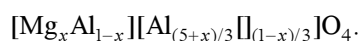


where x is positive and $x \leq 1$.

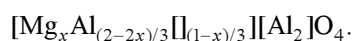
It is to be noted that



represents the form where replacement of some magnesium ions by aluminium ions has taken place at the tetrahedral site. Then, some aluminium ions from octahedral position fill the deficit at the tetrahedral site. This results in cation vacancy at the octahedral position (Gray 1971). Molecular formula containing cation vacancies in octahedral sites can be represented as



If cation vacancies are created in tetrahedral positions, then the form would be



However, as evidence of cation vacancies at the tetrahedral sites for alumina enriched spinels is hardly available, cation vacancies at the octahedral sites have only been investigated.

Both MgAl₂O₄ spinel and γ -Al₂O₃ are isostructural, and therefore it is expected that unit cell parameter of MgAl₂O₄ - γ -Al₂O₃ solid solution would follow additive property. Hence its unit cell parameter a is determined from cell parameters of MgAl₂O₄ and γ -Al₂O₃ following the additive relation as described by Shou-Yong *et al* (2000)

$$a = \frac{[\text{No. of moles of MgAl}_2\text{O}_4 \times a_0 + \text{no. of moles of } \gamma\text{-Al}_2\text{O}_3 \times a_1]}{[\text{No. of moles of MgAl}_2\text{O}_4 + \text{no. of moles of } \gamma\text{-Al}_2\text{O}_3]}$$

$$= \frac{a_0 + \frac{3(n-1)}{4} a_1}{1 + \frac{3(n-1)}{4}},$$

where a_0 = lattice constant of MgAl₂O₄, a_1 = lattice constant of γ -Al₂O₃.

Unit cell parameter a for different values of n has been calculated at 1000°C, 3 h and incorporated in table 2. Experimental values are the same as in table 1 and calculated results have been derived applying the additive relation. It can be clearly seen that experimental and calculated results of lattice constant a decrease with increasing values of n . The present consideration of n values (except for $n = 30$) has close similarity with the one reported by others (Shou-Yong *et al* 2000; Zawrah 2004). Molecular formulae of Mg-Al spinels ($n > 1$) in

terms of substitution at tetrahedral sites and cation vacancies in the octahedral sites have been incorporated in table 3. These results reveal that MgAl₂O₄ can accommodate high amount of γ -Al₂O₃ (as solid solution). It has been observed that Mg-Al spinel ($n = 30$) gives MgAl₂O₄- γ -Al₂O₃ solid solution and γ -Al₂O₃ peaks (figure 1). Therefore, there must be a limit of accommodation of alumina beyond stoichiometry in MgAl₂O₄ structure. Furthermore, Mg-Al spinels having $n > 1$ may not be stable at high temperatures ($\geq 1100^\circ\text{C}$) where $\gamma \rightarrow \alpha$ alumina conversion causes exsolution of alumina beyond stoichiometry from spinel solid solutions. With this consideration, Mg-Al spinel powders ($n \geq 1$) have been calcined at 1200°C, 3 h to evaluate their phases. A mathematical framework for MgAl₂O₄ - γ -Al₂O₃ solid solution interaction has been discussed to review the extent of solid solution of γ -Al₂O₃ in MgAl₂O₄.

3.2 Mathematical framework for MgAl₂O₄ - γ -Al₂O₃ solid solution interaction

Although molecular formula (table 3) for alumina enriched Mg-Al spinels can be easily formulated depending on the value of n , the mathematical framework for the chemical interactions of MgAl₂O₄ - γ -Al₂O₃ solid solution is quite exhaustive. The representative unit cell of spinel i.e. Mg₈Al₁₆O₃₂ has been considered for interaction with γ -Al₂O₃. In the mathematical framework of MgAl₂O₄ - γ -Al₂O₃ interaction, it is assumed that the MgAl₂O₄ is normal spinel (i.e. all the Mg²⁺ ions are in tetrahedral positions). It may be noted that some percentage of inversion occurs in synthetic spinel where the Mg²⁺ ions are present in octahedral positions. However, the mathematical framework for the substitution of 3Mg²⁺ ions by 2Al³⁺ ions in the MgAl₂O₄ - γ -Al₂O₃ solid solution interactions would remain unchanged irrespective of whether Mg²⁺ ions remain in tetrahedral or octahedral sites.

Case 1: In the first case, Mg₅Al₁₈O₃₂ is formed by the interaction of Mg₈Al₁₆O₃₂ and γ -Al₂O₃. The stepwise reactions can be illustrated as

1st step: In Mg₈Al₁₆O₃₂, 3Mg²⁺ ions are replaced by 2Al³⁺ ions of γ -Al₂O₃ forming 3MgO, i.e.

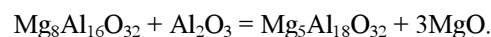


Table 2. Dependence of lattice constant of Mg-Al spinels on the value of n (MgO- n Al₂O₃) at 1000°C, 3 h.

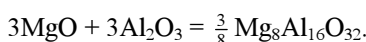
n	Lattice constant (nm)	
	Experimental	Calculated
1-0	0.8072	0.8072
1.5	0.8053	0.8031
3-0	0.7974	0.7981
4-5	0.7964	0.7962

Table 3. Molecular formula of Mg–Al spinels for different n ($\text{MgO}-n\text{Al}_2\text{O}_3$) in terms of substitution at tetrahedral sites and cation vacancies at octahedral sites.

n^*	x^{**}	$[\text{Mg}_x\text{Al}_{2-2x}]_3[\text{Al}_2]\text{O}_4$	$[\text{Mg}_x\text{Al}_{1-x}]_3[\text{Al}_{\frac{5+x}{3}}]_3[\text{Al}_{\frac{1-x}{3}}]\text{O}_4$
1.0	1	MgAl_2O_4	–
1.5	0.73	$[\text{Mg}_{0.73}\text{Al}_{0.18}][\text{Al}_2]\text{O}_4$	$[\text{Mg}_{0.73}\text{Al}_{0.27}][\text{Al}_{\frac{5.73}{3}}][\text{Al}_{\frac{0.27}{3}}]\text{O}_4$
3.0	0.40	$[\text{Mg}_{0.4}\text{Al}_{0.4}][\text{Al}_2]\text{O}_4$	$[\text{Mg}_{0.4}\text{Al}_{0.6}][\text{Al}_{\frac{5.4}{3}}][\text{Al}_{\frac{0.6}{3}}]\text{O}_4$
4.5	0.28	$[\text{Mg}_{0.28}\text{Al}_{0.48}][\text{Al}_2]\text{O}_4$	$[\text{Mg}_{0.28}\text{Al}_{0.72}][\text{Al}_{\frac{5.28}{3}}][\text{Al}_{\frac{0.72}{3}}]\text{O}_4$

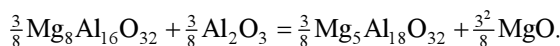
* $\text{MgO}-n\text{Al}_2\text{O}_3$; ** $[\text{Mg}_x\text{Al}_{2-2x}]_3[\text{Al}_2]\text{O}_4$

2nd step: MgO formed combine with Al_2O_3 to form $\text{Mg}_8\text{Al}_{16}\text{O}_{32}$, i.e.

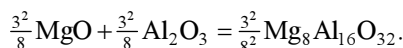


Hence, $3\text{MgAl}_2\text{O}_4$ has been expressed in the form of unit cell of spinel.

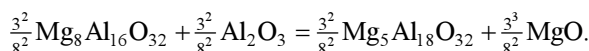
3rd step:



4th step:



5th step:



Similarly, an infinite number of steps follow for each of the unit cells of spinel. Theoretically, although it is assumed that an infinite number of steps occur, but in reality the interaction appears to be nearly complete within the first few steps.

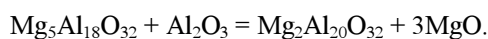
Adding all the steps and rearranging:

$$\begin{aligned} & \text{Mg}_8\text{Al}_{16}\text{O}_{32} + (1 + \frac{3}{8} + \frac{3^2}{8^2} + \dots \infty)\text{Al}_2\text{O}_3 \\ & + 3 \times (1 + \frac{3}{8} + \frac{3^2}{8^2} + \dots \infty)\text{Al}_2\text{O}_3 \\ & = (1 + \frac{3}{8} + \frac{3^2}{8^2} + \dots \infty)\text{Mg}_5\text{Al}_{18}\text{O}_{32} \\ & \Rightarrow \text{Mg}_8\text{Al}_{16}\text{O}_{32} + 6.4\text{Al}_2\text{O}_3 = 1.6\text{Mg}_5\text{Al}_{18}\text{O}_{32}. \quad (1) \end{aligned}$$

Equation (1) is the result of Case 1. The term $\text{Mg}_5\text{Al}_{18}\text{O}_{32}$ can be represented in molar ratios as $\text{MgO}-1.8\text{Al}_2\text{O}_3$ and $\text{MgAl}_2\text{O}_4-0.8\text{Al}_2\text{O}_3$. In terms of cation vacancies of the type in table 3, it becomes $[\text{Mg}_{0.625}\text{Al}_{0.375}][\text{Al}_{1.875}][\text{Al}_{0.125}]\text{O}_4$.

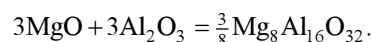
Case 2: In the second case, $\text{Mg}_5\text{Al}_{18}\text{O}_{32}$ further interacts with $\gamma\text{-Al}_2\text{O}_3$ to form $\text{Mg}_2\text{Al}_{20}\text{O}_{32}$. As in Case 1, reaction steps are as follows:

1st step:

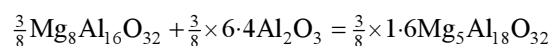


(The coefficient 1.6 of $\text{Mg}_5\text{Al}_{18}\text{O}_{32}$ has been adjusted at the end).

2nd step:



3rd step:



and

$$\begin{aligned} & \frac{3 \times 1.6}{8}\text{Mg}_5\text{Al}_{18}\text{O}_{32} + \frac{3 \times 1.6}{8}\text{Al}_2\text{O}_3 \\ & = \frac{3 \times 1.6}{8}\text{Mg}_2\text{Al}_{20}\text{O}_{32} + 3 \times \left(\frac{3 \times 1.6}{8}\right)\text{MgO}. \end{aligned}$$

4th step:

$$\begin{aligned} & 3 \times \left(\frac{3 \times 1.6}{8}\right)\text{MgO} + 3 \times \left(\frac{3 \times 1.6}{8}\right)\text{Al}_2\text{O}_3 \\ & = \left(\frac{3}{8}\right) \times \left(\frac{3 \times 1.6}{8}\right)\text{Mg}_8\text{Al}_{16}\text{O}_{32} \end{aligned}$$

5th step:

$$\begin{aligned} & \left(\frac{3 \times 1.6}{8}\right) \times \frac{3}{8}\text{Mg}_8\text{Al}_{16}\text{O}_{32} + \left(\frac{3 \times 1.6}{8}\right) \times \left(\frac{3}{8}\right) \times \\ & 6.4\text{Al}_2\text{O}_3 = \left(\frac{3 \times 1.6}{8}\right)^2\text{Mg}_5\text{Al}_{18}\text{O}_{32} \end{aligned}$$

and

$$\begin{aligned} & \left(\frac{3 \times 1.6}{8}\right)^2\text{Mg}_5\text{Al}_{18}\text{O}_{32} + \left(\frac{3 \times 1.6}{8}\right)^2\text{Al}_2\text{O}_3 \\ & = \left(\frac{3 \times 1.6}{8}\right)^2\text{Mg}_2\text{Al}_{20}\text{O}_{32} + \left(\frac{3 \times 1.6}{8}\right)^2 \times 3\text{MgO} \end{aligned}$$

Likewise, an infinite number of steps follow for each of the unit cells of spinel.

Adding these steps and rearranging:

$$\begin{aligned}
 & \text{Mg}_5\text{Al}_{18}\text{O}_{32} + \text{Al}_2\text{O}_3 + \\
 & 3 \times \left[1 + \left(\frac{3 \times 1.6}{8} \right) + \left(\frac{3 \times 1.6}{8} \right)^2 + \dots \infty \right] \text{Al}_2\text{O}_3 \\
 & + \left(\frac{3}{8} \times 6.4 \right) \times \left[1 + \left(\frac{3 \times 1.6}{8} \right) + \left(\frac{3 \times 1.6}{8} \right)^2 + \dots \infty \right] \text{Al}_2\text{O}_3 \\
 & + \left(\frac{3 \times 1.6}{8} \right) \times \left[1 + \left(\frac{3 \times 1.6}{8} \right) + \left(\frac{3 \times 1.6}{8} \right)^2 + \dots \infty \right] \text{Al}_2\text{O}_3 \\
 & = \left[1 + \left(\frac{3 \times 1.6}{8} \right) + \left(\frac{3 \times 1.6}{8} \right)^2 + \dots \infty \right] \text{Mg}_2\text{Al}_{20}\text{O}_{32} \\
 & \Rightarrow \text{Mg}_5\text{Al}_{18}\text{O}_{32} + 16\text{Al}_2\text{O}_3 \\
 & = 2.5\text{Mg}_2\text{Al}_{20}\text{O}_{32} \\
 & \Rightarrow 1.6\text{Mg}_5\text{Al}_{18}\text{O}_{32} + 25.6\text{Al}_2\text{O}_3 = 4\text{Mg}_2\text{Al}_{20}\text{O}_{32}. \quad (2)
 \end{aligned}$$

Adding (1) and (2), result after Case 2 becomes

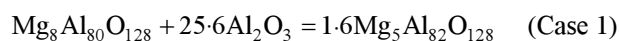
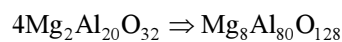
$$\text{Mg}_8\text{Al}_{16}\text{O}_{32} + 32\text{Al}_2\text{O}_3 = 4\text{Mg}_2\text{Al}_{20}\text{O}_{32}. \quad (3)$$

In molar ratios, Mg₂Al₂₀O₃₂ converts to MgO-5Al₂O₃ and MgAl₂O₄-4Al₂O₃, and in terms of cation vacancies as in table 3 it can be represented as:

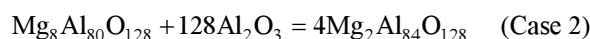


Further substitution of Mg²⁺ by Al³⁺ in the unit cell i.e. Mg₂Al₂₀O₃₂ is complicated because whole number

replacement of Mg²⁺ ions by whole number Al³⁺ ions does not seem to be possible. Theoretically, it may be assumed that this whole number replacement would take place from a combination of 4 unit cells. Similar to Cases 1 and 2, the reaction sequence will follow for the interactions i.e.



and



In MgO-*n*Al₂O₃ format, Mg₅Al₈₂O₁₂₈ and Mg₂Al₈₄O₁₂₈ can be represented as MgO-8.2Al₂O₃ and MgO-21Al₂O₃, respectively. For MgAl₂O₄-(*n*-1)Al₂O₃ format, obviously these are MgAl₂O₄-7.2Al₂O₃ and MgAl₂O₄-20Al₂O₃, respectively.

For the next step of Mg²⁺ substitution by Al³⁺, theoretically 4 units of Mg₂Al₈₄O₁₂₈ (i.e. 16 unit cells of Mg₂Al₂₀O₃₂) would be considered and likewise the process is assumed to continue. However, the stable product of MgAl₂O₄- γ -Al₂O₃ solid solution should still be Mg₂Al₂₀O₃₂ which is the outcome of substitution of 6Mg²⁺ ions by 4Al³⁺ ions in unit cell of MgAl₂O₄ (Mg₈Al₁₆O₃₂). For higher values of *n*, it is difficult to retain the identity of only MgAl₂O₄- γ -Al₂O₃ solid solution at forming temperature. For instance, in the present investigation of MgAl₂O₄- γ -Al₂O₃ solid solution, XRD peaks for *n* = 30 do not clearly indicate the identity of only MgAl₂O₄- γ -Al₂O₃ solid solution but also γ -Al₂O₃.

3.3 1200 °C XRD interpretation

Calcination at 1200°C, 3 h has been considered for major phase separation of alumina (as α -Al₂O₃) from spinel

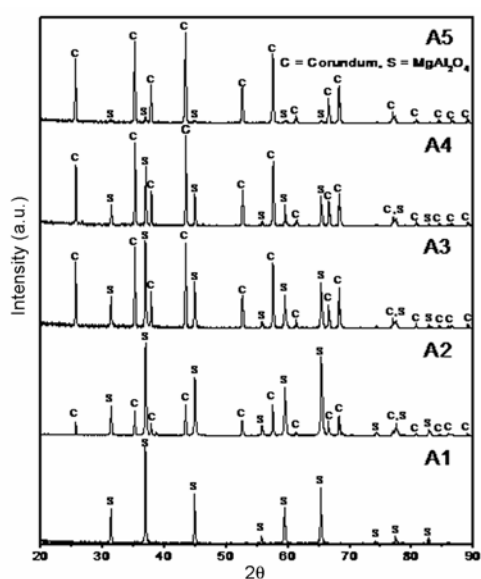


Figure 2. XRD spectra of Mg-Al spinels for $n \geq 1$ (MgO-*n*Al₂O₃) at 1200°C, 3 h.

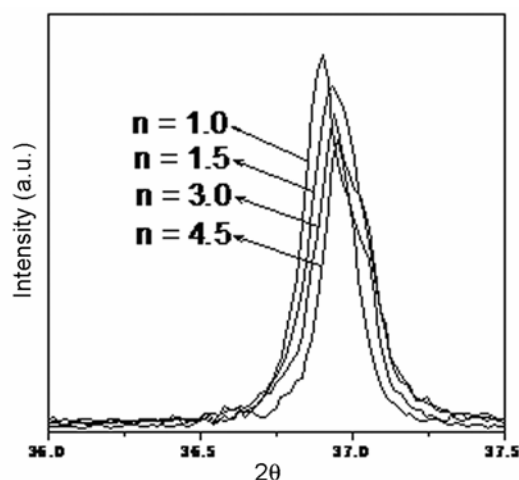


Figure 3. Bragg's angle variation of [113] plane of Mg-Al spinels (MgO-*n*Al₂O₃, $n \geq 1$) at 1200°C, 3 h.

Table 4. Wt% alumina beyond stoichiometry originally present and after phase separation as α -Al₂O₃ for different n (MgO- n Al₂O₃) at 1200°C, 3 h.

n	Wt% Al ₂ O ₃ (original)	Wt% Al ₂ O ₃ (phase separated)
1.0	0.00	0.00
1.5	26.38	24.22
3.0	58.90	56.65
4.5	71.50	71.14
30.0	95.41	95.30

solid solution. XRD curves of Mg–Al spinel powders ($n \geq 1$) at 1200°C, 3 h have been depicted in figure 2. Major phase separation of α -Al₂O₃ can be observed for curves with $n > 1$. Phase quantification has been done by Rietveld analysis and the results are incorporated in table 4. Results reveal that alumina (beyond stoichiometry of spinel) in alumina enriched spinels (1000°C, 3 h) undergo phase transformation (γ -Al₂O₃ \rightarrow α -Al₂O₃) and subsequent phase separation into near stoichiometric MgAl₂O₄ and α -Al₂O₃. Change in Bragg's angle of MgAl₂O₄ peak of [113] plane at 1200°C, 3 h with different n have been plotted in figure 3. Contrary to 1000°C XRD, here, change in Bragg's angle for Mg–Al spinels ($n = 1.5, 3$ and 4.5) is very less compared to stoichiometric spinel ($n = 1$); and consequently change in cell parameter would be negligible. This clearly indicates that Mg–Al spinels ($n > 1$) after 1200°C (3 h) has negligible amount of alumina in spinel as solid solution.

Present investigation suggests that MgAl₂O₄ – γ -Al₂O₃ solid solution (MgO- n Al₂O₃, $n > 1$) powders prepared at 1000°C (3 h) when consolidated into dense products for advanced applications at high temperatures, the final products will not only contain MgAl₂O₄ phase but also exsolved α -Al₂O₃. That means by normal sintering at high temperatures, it is very difficult to produce Mg–Al spinel bodies ($n > 1$) where the alumina present beyond stoichiometry (i.e. α -Al₂O₃) would exist as solid solution in MgAl₂O₄. However, with some process manipulation such as HIP at both high temperature and high forming pressure followed by rapid cooling it is possible to prepare MgAl₂O₄ – α -Al₂O₃ solid solution dense bodies for $n > 1$ (MgO- n Al₂O₃) (Shimada *et al* 1996).

4. Conclusions

(I) MgO–Al₂O₃ binary phase diagram suggests the existence of non-stoichiometric spinel with $n > 1$ (MgO- n Al₂O₃) at high temperatures, where some amount of α -Al₂O₃ goes into solid solution in MgAl₂O₄. However, the solid solution of alumina in MgAl₂O₄ at low temperatures is possible when γ -Al₂O₃ interacts with MgAl₂O₄. In the present work, XRD of 1000°C (3 h) calcined Mg–Al spinels (MgO- n Al₂O₃; $n \geq 1$) indicates only MgAl₂O₄/MgAl₂O₄ – γ -Al₂O₃ solid solution peaks up to $n = 4.5$.

This suggests that alumina present beyond stoichiometry remains as MgAl₂O₄ – γ -Al₂O₃ solid solution.

(II) In each unit cell of spinel (Mg₈Al₁₆O₃₂), MgAl₂O₄ – γ -Al₂O₃ solid solution interaction follows an infinite number of steps theoretically. An attempt has been made to develop a mathematical framework of such interactions based on the substitution of Mg²⁺ ions by Al³⁺ ions in unit cell of MgAl₂O₄. As the extent of substitution increases, combination of unit cells has been suggested to take part. From the mathematical framework, it may be suggested that solid solution for n value (MgO- n Al₂O₃) in the range 1 to 5 is smooth. For $n > 5$ it is suggested that combinations of unit cells take part in the interactions and probably the process gradually becomes complicated.

(III) At 1000°C (3 h), unit cell parameter of non-stoichiometric spinel ($n > 1$) shows the additive property of both γ -Al₂O₃ and MgAl₂O₄. Identity of low temperature MgAl₂O₄ – γ -Al₂O₃ solid solution disappears at higher temperatures as $\gamma \rightarrow \alpha$ alumina phase transformation occurs, and exsolution of α -Al₂O₃ from MgAl₂O₄ solid solution takes place. In the present work, phase separation of α -Al₂O₃ from MgAl₂O₄ solid solution occurs at 1200°C, 3 h.

(IV) As complete MgAl₂O₄ spinel formation ($n = 1$) and solid solution with γ -Al₂O₃ ($n > 1$) can be observed at 1000°C, the coprecipitation technique used in the present investigation is effective to prepare Mg–Al spinels (MgO- n Al₂O₃, $n \geq 1$) for low temperature applications.

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