MgAl$_2$O$_4$–γ-Al$_2$O$_3$ solid solution interaction: mathematical framework and phase separation of α-Al$_2$O$_3$ at high temperature

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Abstract. Although existence of MgAl$_2$O$_4$–γ-Al$_2$O$_3$ 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-Al$_2$O$_3$ in MgAl$_2$O$_4$ (spinel). To investigate the solid solubility of γ-Al$_2$O$_3$ in MgAl$_2$O$_4$, Mg–Al spinel (MgO–nAl$_2$O$_3$; 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 MgAl$_2$O$_4$ phase up to n = 4·5 at 1000°C indicates that alumina (as γ-Al$_2$O$_3$) present beyond stoichiometry gets completely accommodated in MgAl$_2$O$_4$ in the form of solid solution. $\gamma \rightarrow \alpha$ alumina phase transformation and its subsequent separation from MgAl$_2$O$_4$ 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 MgAl$_2$O$_4$ (Mg$_8$Al$_{16}$O$_{32}$) has been considered for the solid solution interactions (substitution of Mg^{2+} ions by Al^{3+} ions) with γ-Al$_2$O$_3$. It is suggested that combination of unit cells of MgAl$_2$O$_4$ takes part in the interactions when $n > 5$ (MgO–nAl$_2$O$_3$).

Keywords. MgAl$_2$O$_4$ spinel; Al$_2$O$_3$; solid solution; phase transformation; X-ray diffraction.

1. Introduction

To achieve phase pure MgAl$_2$O$_4$ (spinel) composition, the primary criteria is to develop a process that would produce precursor powder having Mg^{2+} : Al^{3+} 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 (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 MgAl$_2$O$_4$ spinel is cubic and has 8 formula units of MgAl$_2$O$_4$ with 64 tetrahedral and 32 octahedral sites. All 8 Mg^{2+} ions occupy tetrahedral sites and the 16 Al^{3+} ions are present in octahedral sites. Generally Mg–Al spinels are represented as MgO-nAl$_2$O$_3$: for n = 1 it is stoichio-

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

Synthesis of MgAl$_2$O$_4$–γ-Al$_2$O$_3$ solid solution phases for $n > 1$ (MgO–nAl$_2$O$_3$) 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 MgAl$_2$O$_4$–γ-Al$_2$O$_3$ 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% Al$_2$O$_3$ to 7 wt% MgO. They also revealed phase separation of α-Al$_2$O$_3$ from the solid solution at 1100°C and achieved 100% separation at this temperature in presence of 0·5 wt% α-Al$_2$O$_3$ 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 MgAl$_2$O$_4$ formation, MgAl$_2$O$_4$–γ-Al$_2$O$_3$ solid solution interaction and precipitation of α-Al$_2$O$_3$ from MgAl$_2$O$_4$. A detailed mathematical framework of MgAl$_2$O$_4$–γ-Al$_2$O$_3$ 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 $110°C$ for 48 h. The dried powders were calcined at $1000°$ and $1200°C$ 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 α-Al_2O_3 phases in the powders calcined at $1200°C$, Rietveld analysis was used.
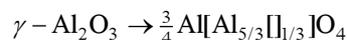
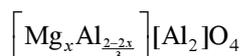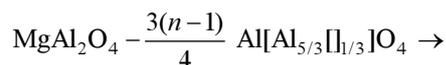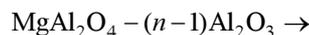## 3. Results and discussion

3.1 *1000°C XRD interpretation*

X-ray spectra of $1000°C$, 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 γ-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 γ-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 γ-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 γ-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 γ-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 ($1000°C$, 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

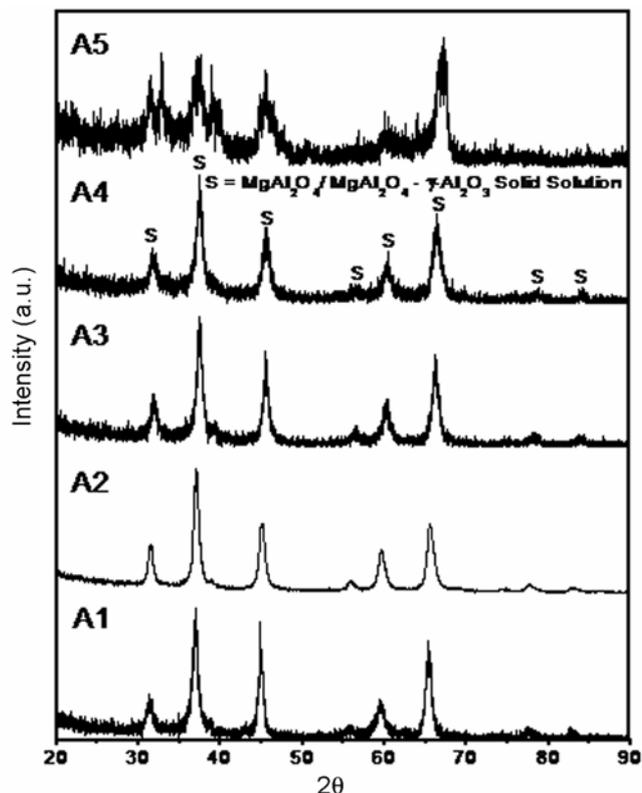parameter. $MgAl_2O_4$–γ-Al_2O_3 solid solution interaction can be represented as

$$MgO - nAl_2O_3 \rightarrow MgAl_2O_4 - (n-1)Al_2O_3,$$

$$\gamma - Al_2O_3 \rightarrow \frac{3}{4}Al[Al_{5/3}[]_{1/3}]O_4$$

and

$$MgAl_2O_4 - (n-1)Al_2O_3 \rightarrow$$

$$MgAl_2O_4 - \frac{3(n-1)}{4}Al[Al_{5/3}[]_{1/3}]O_4 \rightarrow$$

$$\left[Mg_x Al_{\frac{2-2x}{3}} \right][Al_2]O_4$$

where

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


Figure 1. XRD spectra of Mg–Al spinels for $n \geq 1$ (MgO–nAl_2O_3) at $1000°C$, 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 $1000°C$, 3 h.
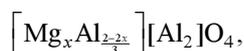
	$n = 1·0$	$n = 1.5$	$n = 3·0$	$n = 4·5$
$2\theta(°)$	36·94	37·02	37·40	37·65
d_{113} (nm)	0·2434	0·2428	0·2404	0·2401
a (nm)	0·8072	0·8053	0·7974	0·7964

Here x has been determined from the equivalence of the relations MgO–nAl$_2$O$_3$ and

$$\left[Mg_x Al_{\frac{2-2x}{3}} \right][Al_2]O_4,$$
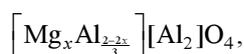
where x is positive and $x \le 1$.

It is to be noted that

$$\left[Mg_x Al_{\frac{2-2x}{3}} \right][Al_2]O_4,$$

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

$$[Mg_x Al_{1-x}][Al_{(5+x)/3}[]_{(1-x)/3}]O_4.$$

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

$$[Mg_x Al_{(2-2x)/3}[]_{(1-x)/3}][Al_2]O_4.$$
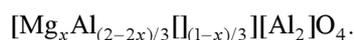
However, as evidence of cation vacancies at the tetrahedral sites for alumina enriched spinels is hardly available, cation vacancies at the octahedral sites have only been investigated.

Both MgAl$_2$O$_4$ spinel and γ-Al$_2$O$_3$ are isostructural, and therefore it is expected that unit cell parameter of MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution would follow additive property. Hence its unit cell parameter a is determined from cell parameters of MgAl$_2$O$_4$ and γ-Al$_2$O$_3$ following the additive relation as described by Shou-Yong *et al* (2000)

$$a = \frac{\begin{bmatrix} \text{No. of moles of } MgAl_2O_4 \times a_0 + \\ \text{no. of moles of } \gamma\text{-}Al_2O_3 \times a_1 \end{bmatrix}}{\begin{bmatrix} \text{No. of moles of } MgAl_2O_4 + \\ \text{no. of moles of } \gamma\text{-}Al_2O_3 \end{bmatrix}}$$

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

where a_0 = lattice constant of MgAl$_2$O$_4$, a_1 = lattice constant of γ-Al$_2$O$_3$.

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 MgAl$_2$O$_4$ can accommodate high amount of γ-Al$_2$O$_3$ (as solid solution). It has been observed that Mg–Al spinel (n = 30) gives MgAl$_2$O$_4$–γ-Al$_2$O$_3$ solid solution and γ-Al$_2$O$_3$ peaks (figure 1). Therefore, there must be a limit of accommodation of alumina beyond stoichiometry in MgAl$_2$O$_4$ structure. Furthermore, Mg–Al spinels having $n > 1$ may not be stable at high temperatures ($\ge$ 1100°C) where γ → α alumina conversion causes exsolution of alumina beyond stoichiometry from spinel solid solutions. With this consideration, Mg–Al spinel powders ($n \ge 1$) have been calcined at 1200°C, 3 h to evaluate their phases. A mathematical framework for MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution interaction has been discussed to review the extent of solid solution of γ-Al$_2$O$_3$ in MgAl$_2$O$_4$.

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 MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution is quite exhaustive. The representative unit cell of spinel i.e. Mg$_8$Al$_{16}$O$_{32}$ has been considered for interaction with γ-Al$_2$O$_3$. In the mathematical framework of MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ interaction, it is assumed that the MgAl$_2$O$_4$ is normal spinel (i.e. all the Mg^{2+} ions are in tetrahedral positions). It may be noted that some percentage of inversion occurs in synthetic spinel where the Mg^{2+} ions are present in octahedral positions. However, the mathematical framework for the substitution of 3Mg^{2+} ions by 2Al^{3+} ions in the MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution interactions would remain unchanged irrespective of whether Mg^{2+} ions remain in tetrahedral or octahedral sites.

Case 1: In the first case, Mg$_5$Al$_{18}$O$_{32}$ is formed by the interaction of Mg$_8$Al$_{16}$O$_{32}$ and γ-Al$_2$O$_3$. The stepwise reactions can be illustrated as

1st step: In Mg$_8$Al$_{16}$O$_{32}$, 3Mg^{2+} ions are replaced by 2Al^{3+} ions of γ-Al$_2$O$_3$ forming 3MgO, i.e.

$$Mg_8Al_{16}O_{32} + Al_2O_3 = Mg_5Al_{18}O_{32} + 3MgO.$$
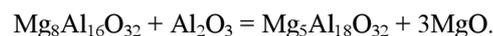
Table 2. Dependence of lattice constant of Mg–Al spinels on the value of n (MgO–nAl$_2$O$_3$) at 1000°C, 3 h.

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 (MgO–nAl$_2$O$_3$) in terms of substitution at tetrahedral sites and cation vacancies at octahedral sites.

n*	x**	$[Mg_xAl_{\frac{2-2x}{3}}][Al_2]O_4$	$[Mg_xAl_{1-x}][Al_{\frac{5+x}{3}}[]_{\frac{1-x}{3}}]O_4$
1·0	1	MgAl$_2$O$_4$	–
1·5	0·73	$[Mg_{0.73}Al_{0.18}][Al_2]O_4$	$[Mg_{0.73}Al_{0.27}][Al_{\frac{5.73}{3}}[]_{\frac{0.27}{3}}]O_4$
3·0	0·40	$[Mg_{0.4}Al_{0.4}][Al_2]O_4$	$[Mg_{0.4}Al_{0.6}][Al_{\frac{5.4}{3}}[]_{\frac{0.6}{3}}]O_4$
4·5	0·28	$[Mg_{0.28}Al_{0.48}][Al_2]O_4$	$[Mg_{0.28}Al_{0.72}][Al_{\frac{5.28}{3}}[]_{\frac{0.72}{3}}]O_4$

*MgO–nAl$_2$O$_3$; **$[Mg_xAl_{\frac{2-2x}{3}}][Al_2]O_4$

2nd step: MgO formed combine with Al$_2$O$_3$ to form Mg$_8$Al$_{16}$O$_{32}$, i.e.

$$3MgO + 3Al_2O_3 = \tfrac{3}{8}Mg_8Al_{16}O_{32}.$$
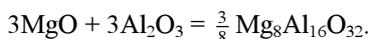
Hence, 3MgAl$_2$O$_4$ has been expressed in the form of unit cell of spinel.

3rd step:

$$\tfrac{3}{8}Mg_8Al_{16}O_{32} + \tfrac{3}{8}Al_2O_3 = \tfrac{3}{8}Mg_5Al_{18}O_{32} + \tfrac{3^2}{8}MgO.$$

4th step:

$$\tfrac{3^2}{8}MgO + \tfrac{3^2}{8}Al_2O_3 = \tfrac{3^2}{8^2}Mg_8Al_{16}O_{32}.$$

5th step:

$$\tfrac{3^2}{8^2}Mg_8Al_{16}O_{32} + \tfrac{3^2}{8^2}Al_2O_3 = \tfrac{3^2}{8^2}Mg_5Al_{18}O_{32} + \tfrac{3^3}{8^2}MgO.$$
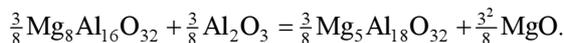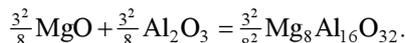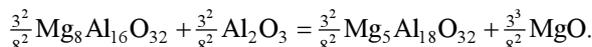
Similarly, an infinite number of steps follow for each of the unit cells of spinel. Theoretically, although it is assumed that an infinite number of steps occur, but in reality the interaction appears to be nearly complete within the first few steps.

Adding all the steps and rearranging:

$$Mg_8Al_{16}O_{32} + (1 + \tfrac{3}{8} + \tfrac{3^2}{8^2} + ...\infty)Al_2O_3$$

$$+ 3 \times (1 + \tfrac{3}{8} + \tfrac{3^2}{8^2} + ...\infty)Al_2O_3$$

$$= (1 + \tfrac{3}{8} + \tfrac{3^2}{8^2} + ...\infty)Mg_5Al_{18}O_{32}$$

$$\Rightarrow Mg_8Al_{16}O_{32} + 6.4Al_2O_3 = 1.6Mg_5Al_{18}O_{32}. \qquad (1)$$

Equation (1) is the result of Case 1. The term Mg$_5$Al$_{18}$O$_{32}$ can be represented in molar ratios as MgO–1·8Al$_2$O$_3$ and MgAl$_2$O$_4$–0·8Al$_2$O$_3$. In terms of cation vacancies of the type in table 3, it becomes $[Mg_{0.625}Al_{0.375}][Al_{1.875}[]_{0.125}]O_4$.

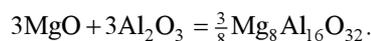*Case 2*: In the second case, Mg$_5$Al$_{18}$O$_{32}$ further interacts with γ-Al$_2$O$_3$ to form Mg$_2$Al$_{20}$O$_{32}$. As in Case 1, reaction steps are as follows:

1st step:

$$Mg_5Al_{18}O_{32} + Al_2O_3 = Mg_2Al_{20}O_{32} + 3MgO.$$
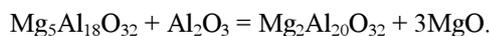
(The coefficient 1·6 of Mg$_5$Al$_{18}$O$_{32}$ has been adjusted at the end).

2nd step:

$$3MgO + 3Al_2O_3 = \tfrac{3}{8}Mg_8Al_{16}O_{32}.$$

3rd step:

$$\tfrac{3}{8}Mg_8Al_{16}O_{32} + \tfrac{3}{8} \times 6.4 Al_2O_3 = \tfrac{3}{8} \times 1.6 Mg_5Al_{18}O_{32}$$

and

$$\frac{3 \times 1.6}{8}Mg_5Al_{18}O_{32} + \frac{3 \times 1.6}{8}Al_2O_3$$

$$= \frac{3 \times 1.6}{8}Mg_2Al_{20}O_{32} + 3 \times \left(\frac{3 \times 1.6}{8}\right)MgO.$$

4th step:

$$3 \times \left(\frac{3 \times 1.6}{8}\right)MgO + 3 \times \left(\frac{3 \times 1.6}{8}\right)Al_2O_3$$

$$= \left(\frac{3}{8}\right) \times \left(\frac{3 \times 1.6}{8}\right)Mg_8Al_{16}O_{32}$$

5th step:

$$\left(\frac{3 \times 1.6}{8}\right) \times \frac{3}{8}Mg_8Al_{16}O_{32} + \left(\frac{3 \times 1.6}{8}\right) \times \left(\frac{3}{8}\right) \times$$

$$6.4Al_2O_3 = \left(\frac{3 \times 1.6}{8}\right)^2 Mg_5Al_{18}O_{32}$$

and

$$\left(\frac{3 \times 1.6}{8}\right)^2 Mg_5Al_{18}O_{32} + \left(\frac{3 \times 1.6}{8}\right)^2 Al_2O_3$$

$$= \left(\frac{3 \times 1.6}{8}\right)^2 Mg_2Al_{20}O_{32} + \left(\frac{3 \times 1.6}{8}\right)^2 \times 3MgO$$

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

Adding these steps and rearranging:

$$\mathrm{Mg_5Al_{18}O_{32} + Al_2O_3 +}$$

$$3 \times \left[1 + \left(\frac{3 \times 1{\cdot}6}{8}\right) + \left(\frac{3 \times 1{\cdot}6}{8}\right)^2 + \ldots \infty\right] \mathrm{Al_2O_3}$$

$$+ \left(\frac{3}{8} \times 6{\cdot}4\right) \times \left[1 + \left(\frac{3 \times 1{\cdot}6}{8}\right) + \left(\frac{3 \times 1{\cdot}6}{8}\right)^2 + \ldots \infty\right] \mathrm{Al_2O_3}$$

$$+ \left(\frac{3 \times 1{\cdot}6}{8}\right) \times \left[1 + \left(\frac{3 \times 1{\cdot}6}{8}\right) + \left(\frac{3 \times 1{\cdot}6}{8}\right)^2 + \ldots \infty\right] \mathrm{Al_2O_3}$$

$$= \left[1 + \left(\frac{3 \times 1{\cdot}6}{8}\right) + \left(\frac{3 \times 1{\cdot}6}{8}\right)^2 + \ldots \infty\right] \mathrm{Mg_2Al_{20}O_{32}}$$

$$\Rightarrow \mathrm{Mg_5Al_{18}O_{32} + 16Al_2O_3}$$

$$= 2{\cdot}5\,\mathrm{Mg_2Al_{20}O_{32}}$$

$$\Rightarrow 1{\cdot}6\,\mathrm{Mg_5Al_{18}O_{32} + 25{\cdot}6Al_2O_3 = 4Mg_2Al_{20}O_{32}}. \quad (2)$$

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

$$\mathrm{Mg_8Al_{16}O_{32} + 32Al_2O_3 = 4Mg_2Al_{20}O_{32}}. \quad (3)$$

In molar ratios, $\mathrm{Mg_2Al_{20}O_{32}}$ converts to $\mathrm{MgO-5Al_2O_3}$ and $\mathrm{MgAl_2O_4-4Al_2O_3}$, and in terms of cation vacancies as in table 3 it can be represented as:

$$\left[\mathrm{Mg_{0{\cdot}25}Al_{0{\cdot}75}}\right]\left[\mathrm{Al_{1{\cdot}75}\square_{0{\cdot}25}}\right]\mathrm{O_4}.$$

Further substitution of $\mathrm{Mg^{2+}}$ by $\mathrm{Al^{3+}}$ in the unit cell i.e. $\mathrm{Mg_2Al_{20}O_{32}}$ is complicated because whole number replacement of $\mathrm{Mg^{2+}}$ ions by whole number $\mathrm{Al^{3+}}$ 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.

$$4\mathrm{Mg_2Al_{20}O_{32}} \Rightarrow \mathrm{Mg_8Al_{80}O_{128}}$$

$$\mathrm{Mg_8Al_{80}O_{128} + 25{\cdot}6Al_2O_3 = 1{\cdot}6Mg_5Al_{82}O_{128}} \quad \text{(Case 1)}$$

and

$$\mathrm{Mg_8Al_{80}O_{128} + 128Al_2O_3 = 4Mg_2Al_{84}O_{128}} \quad \text{(Case 2)}$$
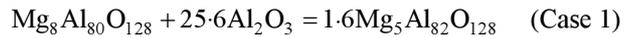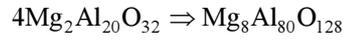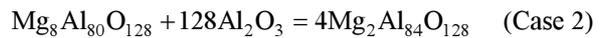
In MgO–$n\mathrm{Al_2O_3}$ format, $\mathrm{Mg_5Al_{82}O_{128}}$ and $\mathrm{Mg_2Al_{84}O_{128}}$ can be represented as $\mathrm{MgO-8{\cdot}2Al_2O_3}$ and $\mathrm{MgO-21Al_2O_3}$, respectively. For $\mathrm{MgAl_2O_4}$–$(n-1)\mathrm{Al_2O_3}$ format, obviously these are $\mathrm{MgAl_2O_4-7{\cdot}2Al_2O_3}$ and $\mathrm{MgAl_2O_4-20Al_2O_3}$, respectively.

For the next step of $\mathrm{Mg^{2+}}$ substitution by $\mathrm{Al^{3+}}$, theoretically 4 units of $\mathrm{Mg_2Al_{84}O_{128}}$ (i.e. 16 unit cells of $\mathrm{Mg_2Al_{20}O_{32}}$) would be considered and likewise the process is assumed to continue. However, the stable product of $\mathrm{MgAl_2O_4-\gamma\text{-}Al_2O_3}$ solid solution should still be $\mathrm{Mg_2Al_{20}O_{32}}$ which is the outcome of substitution of $6\mathrm{Mg^{2+}}$ ions by $4\mathrm{Al^{3+}}$ ions in unit cell of $\mathrm{MgAl_2O_4}$ ($\mathrm{Mg_8Al_{16}O_{32}}$). For higher values of n, it is difficult to retain the identity of only $\mathrm{MgAl_2O_4-\gamma\text{-}Al_2O_3}$ solid solution at forming temperature. For instance, in the present investigation of $\mathrm{MgAl_2O_4-\gamma\text{-}Al_2O_3}$ solid solution, XRD peaks for $n = 30$ do not clearly indicate the identity of only $\mathrm{MgAl_2O_4-\gamma\text{-}Al_2O_3}$ solid solution but also $\gamma\text{-}\mathrm{Al_2O_3}$.

3.3 *1200°C XRD interpretation*

Calcination at 1200°C, 3 h has been considered for major phase separation of alumina (as $\alpha\text{-}\mathrm{Al_2O_3}$) from spinel
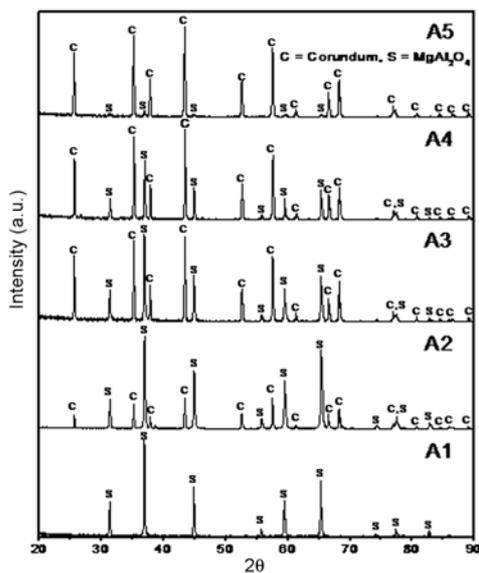
Figure 2. XRD spectra of Mg–Al spinels for $n \geq 1$ (MgO–$n\mathrm{Al_2O_3}$) at 1200°C, 3 h.
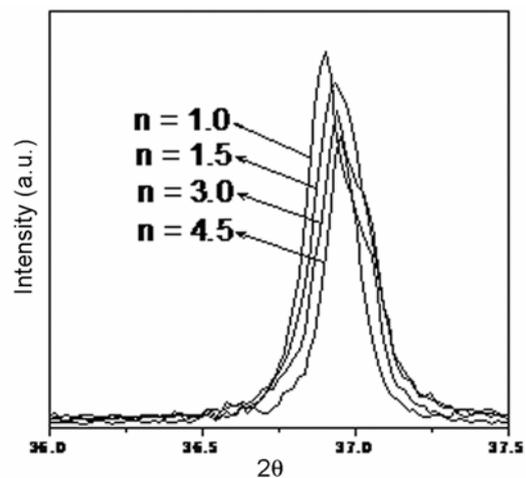
Figure 3. Bragg's angle variation of [113] plane of Mg–Al spinels (MgO–$n\mathrm{Al_2O_3}$, $n \geq 1$) at 1200°C, 3 h.

Table 4. Wt% alumina beyond stoichiometry originally present and after phase separation as α-Al$_2$O$_3$ for different n (MgO–nAl$_2$O$_3$) 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-Al$_2$O$_3$ 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-Al$_2$O$_3$ → α-Al$_2$O$_3$) and subsequent phase separation into near stoichiometric MgAl$_2$O$_4$ and α-Al$_2$O$_3$. Change in Bragg's angle of MgAl$_2$O$_4$ 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 MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution (MgO–nAl$_2$O$_3$, $n > 1$) 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 MgAl$_2$O$_4$ phase but also exsolved α-Al$_2$O$_3$. 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-Al$_2$O$_3$) would exist as solid solution in MgAl$_2$O$_4$. 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 MgAl$_2$O$_4$ – α-Al$_2$O$_3$ solid solution dense bodies for $n > 1$ (MgO–nAl$_2$O$_3$) (Shimada *et al* 1996).

4. Conclusions

(I) MgO–Al$_2$O$_3$ binary phase diagram suggests the existence of non-stoichiometric spinel with $n > 1$ (MgO–nAl$_2$O$_3$) at high temperatures, where some amount of α-Al$_2$O$_3$ goes into solid solution in MgAl$_2$O$_4$. However, the solid solution of alumina in MgAl$_2$O$_4$ at low temperatures is possible when γ-Al$_2$O$_3$ interacts with MgAl$_2$O$_4$. In the present work, XRD of 1000°C (3 h) calcined Mg–Al spinels (MgO–nAl$_2$O$_3$; $n \geq 1$) indicates only MgAl$_2$O$_4$/ MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution peaks up to $n = 4.5$.

This suggests that alumina present beyond stoichiometry remains as MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution.
(II) In each unit cell of spinel (Mg$_8$Al$_{16}$O$_{32}$), MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ 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 Mg^{2+} ions by Al^{3+} ions in unit cell of MgAl$_2$O$_4$. 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–nAl$_2$O$_3$) 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-Al$_2$O$_3$ and MgAl$_2$O$_4$. Identity of low temperature MgAl$_2$O$_4$ – γ-Al$_2$O$_3$ solid solution disappears at higher temperatures as $\gamma \rightarrow \alpha$ alumina phase transformation occurs, and exsolution of α-Al$_2$O$_3$ from MgAl$_2$O$_4$ solid solution takes place. In the present work, phase separation of α-Al$_2$O$_3$ from MgAl$_2$O$_4$ solid solution occurs at 1200°C, 3 h.
(IV) As complete MgAl$_2$O$_4$ spinel formation ($n = 1$) and solid solution with γ-Al$_2$O$_3$ ($n > 1$) can be observed at 1000°C, the coprecipitation technique used in the present investigation is effective to prepare Mg–Al spinels (MgO–nAl$_2$O$_3$, $n \geq 1$) for low temperature applications.

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