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A new sintering aid for magnesium aluminate spinel

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Abstract

A dense $MgAl_2O_4$ sintered spinel has been prepared following a conventional double stage firing process. A new type of sintering aid, $AlCl_3$, can improve the bulk density, apparent porosity and water absorption of $MgAl_2O_4$ spinel sintered at 1550°C devoid of any contamination. In order to see the effect of $AlCl_3$ on densification and formation of a $MgAl_2O_4$ spinel, 0.01–0.03 mol% $AlCl_3$ was added separately prior to calcination, subsequent to calcination as well as simultaneously at both stages. $AlCl_3$ is found to be equally effective in enhancing spinel formation during calcination as well as in increasing sintered density. The efficacy of $AlCl_3$ as a "spinelizer" or as a sintering aid is also compared with the conventional mineralizer, AlF_3, which is generally added only prior to calcination to enhance the spinel formation. $AlCl_3$ is found to be active as a sintering aid provided the powder contains some free Al_2O_3 and MgO and probably the hygroscopic nature of $AlCl_3$ is responsible for its effectiveness as a sintering aid. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: $MgAl_2O_4$ spinel; Double stage sintering; Sintering aid; $AlCl_3$

1. Introduction

Magnesium aluminate spinel (MAS) possesses a unique combination of desirable properties such as high melting point, high strength at elevated temperature, high chemical inertness, low thermal expansion coefficient and high thermal shock resistance to make it an excellent refractory material which is used in cement rotary kilns, lining of steel ladles, glass tank furnaces and other ceramic applications [1–5]. In addition, $MgAl_2O_4$ spinel exhibits first deformation under 0.2 MPa at 2000°C, does not react with silica until 1737°C, CaO or MgO until 2000°C, α-Al_2O_3 until 1927°C, and can be used for all metals except alkaline earth [6]. Due to its eco-friendly nature, unlike magnesia-chrome based refractories [7], the later ones are constantly being replaced by $MgAl_2O_4$ spinels [8]. In spite of these advantages, there are some practical problems encountered in the production of magnesium aluminate spinel bodies. During $MgAl_2O_4$ spinel formation from its constituents, there is a significant amount of volume expansion (about 8%) [9] and on account of this expansion it is very difficult to obtain a dense $MgAl_2O_4$ spinel body in a single stage firing process. Among the few commercially exploited processes, a double stage firing process has received much attention for the preparation of high purity dense MAS even though it is an expensive process. In this process, in order to reduce or eliminate the volume expansion, the $MgAl_2O_4$ spinel is first synthesized by prior calcination of the raw materials at around 1400°C to get an appreciable amount of spinel phase to overcome the volume expansion barrier and then sintered into a dense magnesium aluminate spinel body [9,10]. However, these high calcination temperatures impede the formation of dense high-purity spinel bodies [11]. Addition of mineralizers such as, V_2O_5, Y_2O_3 [12,13], NaCl and $MgCl_2$ [14,15] can help in reducing this temperature to some extent. In most cases, the spinel so obtained has a low reactivity and requires high sintering temperatures (>1700°C) to form a dense product. Bekker and Lindsay [16] have shown that the addition of aluminum fluoride even in small amounts (i.e. 1–3 wt.%) to uncalcined raw mix could remarkably enhance the conversion of spinel at 1300°C and increase the sinterability leading to higher bulk density. But this process involves extensive grinding as well as a high sintering temperature up to 1650°C. Further, the reduction of sintering temperature by using various sintering aids like TiO_2, B_2O_3, LiF, ZnF_2, BaF_2, CaF_2 [17] and

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Fe_2O_3, CaO [18] in order to facilitate liquid phase sintering have also been studied. However, use of these additives contaminates the product and restricts its application to low temperatures. In all the above mentioned processes, the additives have been incorporated either in the raw-mixture to improve the degree of the spinel formation on calcination or to the calcined material as a sintering aid to reduce the sintering temperature. Nevertheless, these processes have some limitations such as sensitivity to specific raw materials, requirement of fine grinding, high sintering temperatures (>1650°C), tendency to contaminate the product, etc. [16–18].

In the present investigation $AlCl_3$ has been effectively used as a low temperature sintering aid to improve the sintered properties of magnesium aluminate spinel. Further, the effect of $AlCl_3$ as a sintering aid and also as a mineralizer for enhancing spinel formation has been compared with that of AlF_3, a conventional mineralizer which is generally added only before calcination. Finally, a plausible mechanism has been proposed to explain the influence of $AlCl_3$ as a sintering aid.

2. Experimental

2.1. Sample preparation

Commercial aluminum trihydroxide (NALCO, NSPH-10, India) made according to the Bayer process, was used as the aluminum raw material and caustic MgO (Birla Periclase, India), made from sea water magnesia, was used as the magnesia raw material. Their physico-chemical properties are given in Table 1. Aluminum chloride (Loba Chemie, AR Grade, India) and AlF_3 (Rolex, AR Grade, India) were used as mineralizers.

Stoichiometric $MgAl_2O_4$ spinel was prepared according to a typical double stage firing process [2,3,16]. Required quantities of aluminum trihydroxide and caustic MgO were co-ground in a jar mill for 3–4 h. From the ground mixture nodules were made using polyvinyl alcohol (PVA) solution (5 wt.%) followed by oven drying at 125°C overnight. The dried nodules were calcined at 1300°C for 1 h. In order to see the effect of the mineralizer on the spinel formation during calcination, $AlCl_3$ or AlF_3 (0.01–0.03 mole% with respect to the final MAS) were added to the PVA solution, which was used for making nodules. All calcined powders were ground separately in a ball mill for about 6 h under identical conditions and the resultant fine powders were granulated using PVA solution (5 wt.%). In order to incorporate $AlCl_3$ or AlF_3 (0.01–0.03 mol%) as a sintering aid, the requisite amount of it was added to the PVA solution which was used for granulation. All the granules were then dry-pressed in the form of pellets (30 mm dia. × 10 mm height) under the pressure of 196 MPa and sintered at different temperatures ranging from 1500–1650°C for 1 h in an electric furnace.

Table 1
Physico-chemical properties of raw materials

Material	Al $(OH)_3$	Caustic MgO
Al_2O_3 (%)	64.5	–
MgO (%)	–	82.86
Na_2O (%)	0.3	0.093
CaO (%)	0.03	0.908
SiO_2 (%)	0.009	0.97
Fe_2O_3 (%)	0.007	0.106
LOI (RT-1000°C)	34.5	15.5
Specific gravity (g/cc)	2.42	3.58
Average particle size (μm)	85	5.22

2.2. Material characterization

Bulk density, apparent porosity and water absorption were measured according to Archimedes principle using a Mettler balance with attachment (AG 245, Mettler Toledo, Switzerland). Phase analysis of the sample was carried out by X-ray diffraction (PW 1830, Philips, Netherland) using Cu-K_α radiation. Relative phase compositions of samples were calculated from the areas under the maximum intensity peak of the respective phases [19]. Particle sizes of calcined powders were measured (Granulometer G 920, Cilas, France). The microstructure of dense spinel grains was examined using scanning electron microscope (JSM- 5410, Jeol, Japan) with an energy dispersive scanning (Sigma 3.42 Quaser, Kevex, USA) attachment for qualitative and quantitative micro analysis.

3. Results and discussion

3.1. Effect of $AlCl_3$ and AlF_3 as spinelizers

The X-ray diffraction patterns of calcined mixtures of $Al(OH)_3$ and caustic MgO at 1300°C for 1 h in presence of $AlCl_3$ and AlF_3 are shown in Figs. 1 and 2, respectively. As can be seen from Figs. 1 and 2, the extent of spinel formation without any additive is about 82% which increases to 100% with the addition of $AlCl_3$ or AlF_3. However, the amount of additive necessary for complete spinel formation is different for different additives. In the case of $AlCl_3$, 0.03 mol% with respect to the final MAS is adequate for complete spinel formation, however, in the case of AlF_3 it is 0.01 mol% only. This clearly demonstrates the efficacy of AlF_3 as compared to $AlCl_3$. Bakker and Lindsay [16] have also observed a similar influence of AlF_3 on spinel formation, where aluminum fluoride enhances the $\gamma \rightarrow \alpha$ transition in alumina. It also promotes crystal growth of α-alumina during calcination [20]. The same mechanism may also be operative for $AlCl_3$. One of the main

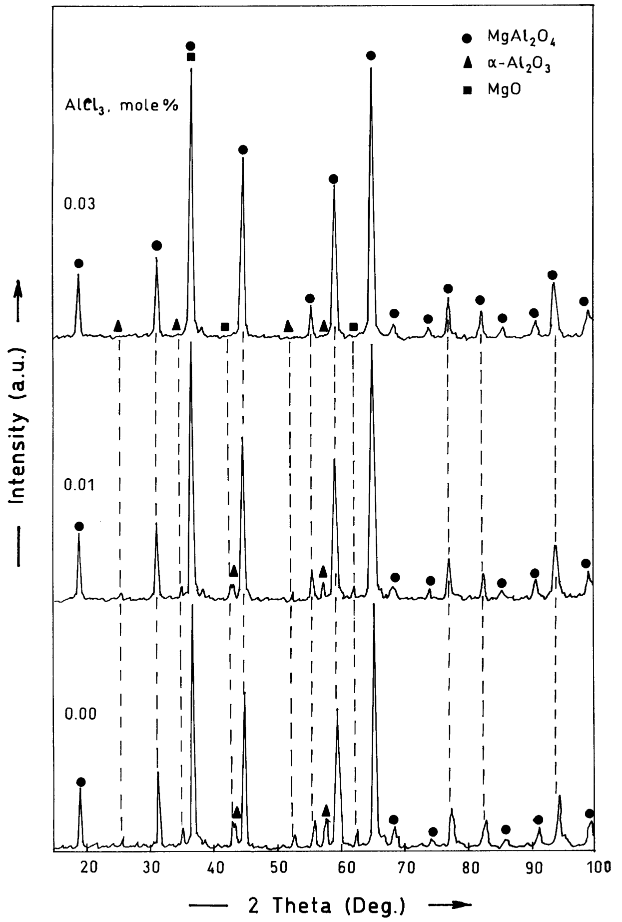


Fig. 1. X-ray powder diffraction patterns of calcined powders obtained from calcination of a raw mixture of Al(OH)$_3$ and caustic MgO at 1300°C for 1 h in the presence of different amounts of $AlCl_3$.

advantages of $AlCl_3$ or AlF_3 as an additive is that during calcination both pyrohydrolyze into Al_2O_3 and gaseous HCl and HF, respectively. Therefore, these mineralizers do not contaminate the $MgAl_2O_4$ spinel product.

It is interesting to note that besides influencing the spinel formation, these mineralizers also have a significant effect on the particle sizes of the calcined powders. When the raw mixture was calcined with AlF_3, the nodules were hard and difficult to crush. However, the powders were friable in the presence of $AlCl_3$ or in the absence of any additive. This phenomenon is clearly manifested as shown in Fig. 3 where the particle size distribution of the powders calcined with and without additives are shown. Probably, the reactions between the impurities like Na_2O, SiO_2, etc., in the raw materials and AlF_3, leads to formation of some low melting phases (sodium fluoride, sodium silico-fluoride, etc.) which results in the formation of agglomerates. In order to evaluate the effect of degree of spinel formation on the densification properties, the calcined powders were ground and sintered at different temperatures. The obtained results are listed in Table 2.

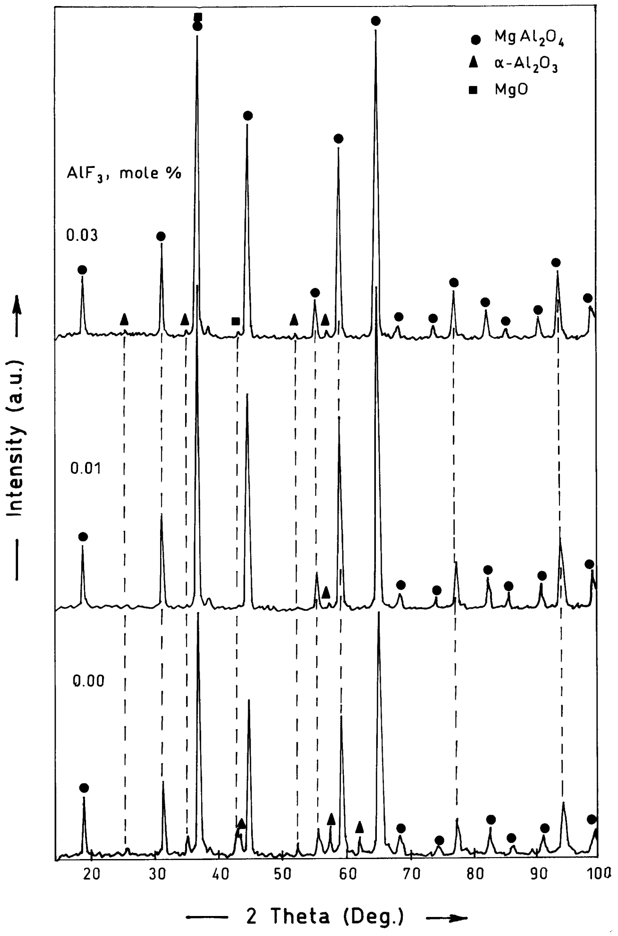


Fig. 2. X-ray powder diffraction patterns of calcined powders obtained from calcination of a raw mixture of Al(OH)$_3$ and caustic MgO at 1300°C for 1 h in the presence of different amounts of AlF_3.

As can be seen from Table 2, the spinel formation has a minor effect on the green density, which increases with an increase in the spinel formation. But as far as sintering is concerned there is hardly any improvement in bulk density, apparent porosity, and water absorption with the increase in spinel formation. If 1600°C is used as the sintering temperature, all the powders can be sintered with excellent sintered properties irrespective of the amount of spinel formation in the starting powder. However, at 1550°C there is only a 5–6% increase in bulk density for fully "spinelized" powder when compared with 82% "spinelized" one. But their poor apparent porosity and water absorption restrict their use in actual application. The overall impression one can get from this table is that a spinel formation of around 80% is sufficient to get a dense product if a proper sintering temperature (~1600°C) is used [10,11].

3.2. *Effect of $AlCl_3$ and AlF_3 as sintering aids*

Based on the above discussion it appears that it is very difficult to sinter magnesium aluminate spinel to a

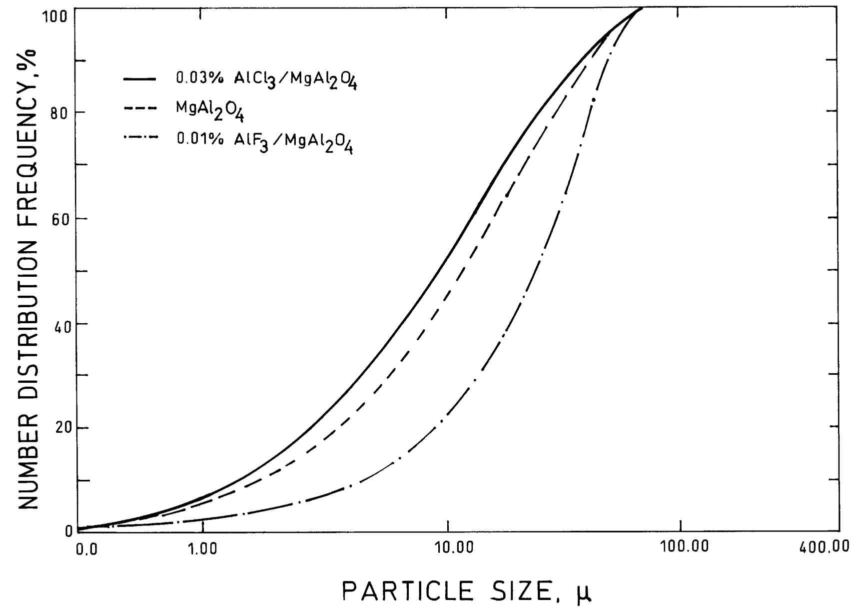


Fig. 3. Particle size distribution of calcined powder obtained from calcination of a raw mixture of $Al(OH)_3$ and caustic MgO at 1300°C for 1 h in the presence of 0.03 mol% of $AlCl_3$ (—), without any additive (- - - -) and with 0.01 mol% AlF_3 (– · –).

Table 2
Properties of MAS sintered at different temperatures in the presence of different amounts of $AlCl_3$ and AlF_3 added before calcination at 1300°C for 1 h

Sample no.	Sample description	Amount of spinelization (%)	Green density (g/cc)	1500°C			1550°C			1600°C		
				BD (g/cc)	AP (%)	WA (%)	BD (g/cc)	AP (%)	WA (%)	BD (g/cc)	AP (%)	WA (%)
1.	$Al(OH)_3+MgO$	82	1.92	2.611	26.42	10.11	3.10	9.97	3.21	3.460	0.012	0.003
2.	$Al(OH)_3+MgO+$ 0.01 mol% $AlCl_3$	90.1	1.98	2.771	20.81	7.511	3.21	5.43	3.25	3.464	0.168	0.048
3.	$Al(OH)_3+MgO+$ 0.03 mol% $AlCl_3$	98.9	2.10	2.801	19.76	6.932	3.25	5.01	4.12	3.459	0.210	0.061
4.	$Al(OH)_3+MgO+$ 0.01 mol% AlF_3	98.0	2.03	2.643	24.33	9.203	3.119	7.66	8.47	3.449	0.134	0.038
5.	$Al(OH)_3+MgO+$ 0.03 mol% AlF_3	98.9	2.09	2.641	22.11	8.139	3.096	8.56	8.91	3.447	0.138	0.046

required density of >3.35 g/cc at less than 1600°C despite the use of 100% spinelized powder. In order to find out the effect of $AlCl_3$ or AlF_3 as a sintering aid, 82% "spinelized" and ground powder (where no additive was used for the spinel formation) was taken and mixed with different amounts of $AlCl_3$ or AlF_3 before sintering it in the form of pressed pellets at various temperatures ranging from 1500–1600°C with a soaking time of 1 h. In general, as the sintering temperature is increased, the sintered properties of MAS spinel body are also found to increase irrespective of the nature or amount of sintering aid. The sintered properties obtained by sintering of MAS containing either $AlCl_3$ or AlF_3 at 1550°C for 1 h are shown in Fig. 4 as a function of the percentage of sintering aids.

As can be seen from Fig. 4, AlF_3 is not useful as a sintering aid but $AlCl_3$ improves bulk density, apparent porosity and water absorption. In fact, in the presence of 0.03 mol% $AlCl_3$, MAS can be sintered to a bulk density of 3.40 g/cc, an apparent porosity of 0.193%, and a water absorption of 0.057% even at a sintering temperature as low as 1550°C for 1 h. The improved sintering in the presence of $AlCl_3$ as a sintering aid is also confirmed by SEM micrographs of fractured surfaces of MAS sintered at 1550°C for 1 h in the presence of $AlCl_3$, without any additive and in the presence of AlF_3 respectively (Fig. 5a–c). It is worth mentioning that 0.03 mol% $AlCl_3$ are sufficient to sinter MAS with appreciable density even when it is added to partially "spinelized" (82%) powder. In view of this it was thought that a further increase of the sintered properties might be possible if $AlCl_3$ could be added to fully "spinelized" powder. For this purpose, 0.03 mol% of $AlCl_3$ was added separately to two fully "spinelized" powders, obtained by the addition of 0.03 mol% $AlCl_3$ and 0.01 mol% AlF_3, respectively in the raw mix prior to calcination. The sintering properties after sintering at 1550°C for 1 h are given in Table 3. For a better comparison the results

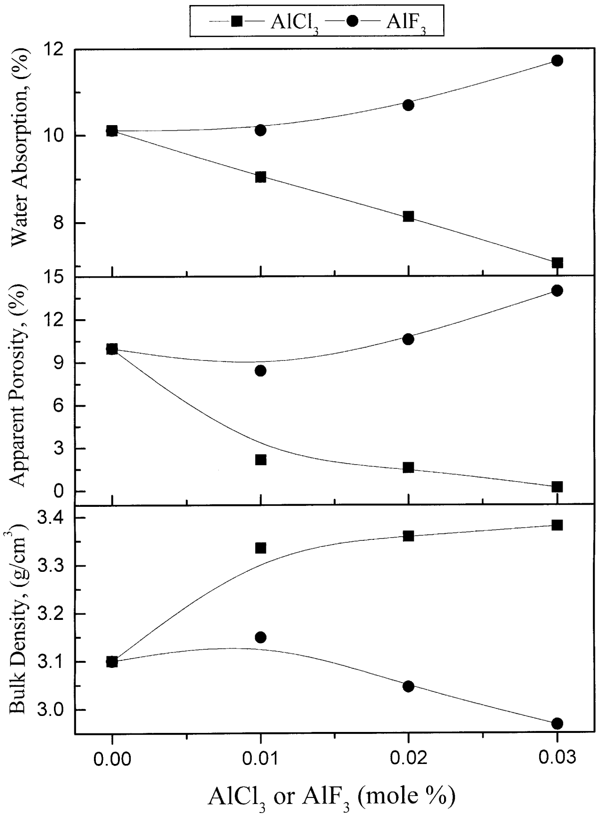


Fig. 4. Variation of bulk density, apparent porosity and water absorption of sintered MAS at 1550°C for 1 h as a function of the amount of $AlCl_3$ and AlF_3.

obtained by the addition of 0.03 mol% $AlCl_3$ as a sintering aid to partially "spinelized" powder is also listed in Table 3. These results undoubtedly suggest that $AlCl_3$ is not effective as a sintering aid if it is added to fully "spinelized" powders. The results also imply that the presence of some amounts of free or unreacted alumina and magnesia are essential in order to make $AlCl_3$ an effective sintering aid in the magnesium aluminate spinel.

3.3. *Plausible mechanism regarding the role of $AlCl_3$ as a sintering aid*

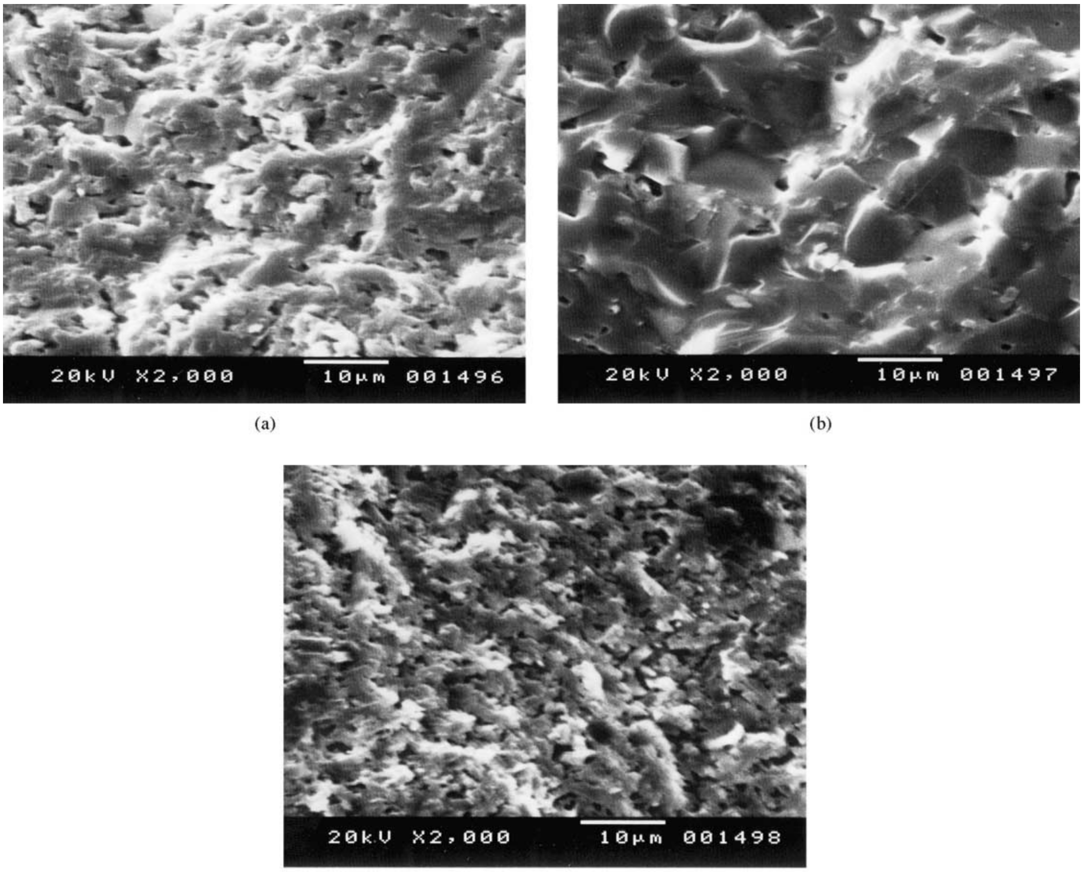
There are several factors, which may influence the sintering behavior of $MgAl_2O_4$ spinel when $AlCl_3$ is incorporated as a sintering aid. Among them, seeding effect, liquid phase sintering due to the formation of a low melting phase in the presence of Cl^- and finally the role of moisture could be considered. At elevated temperatures, both $AlCl_3$ and AlF_3 pyrohydrolyze to yield α-Al_2O_3 and HX, where X^- is either Cl^- or F^-. Similarly, aluminum hydroxide during calcination at above 1000°C is converted into α-Al_2O_3 which on further reaction with periclase form $MgAl_2O_4$ spinel at temperatures higher than 1100°C [9]. It is known that, dopants like AlF_3 accelerate the facile generation of α-Al_2O_3 from its precursors [16,20] which in turn results in a spinel formation at relatively lower calcination temperatures. If this is the reason for enhancing the sintered properties of $MgAl_2O_4$ spinel when doped with $AlCl_3$, the same effect should be observed when doped with AlF_3 as well. But this does not occur. Furthermore, $AlCl_3$ is found to be active only in the presence of sufficient amounts of unreacted alumina and magnesia, which can be considered as seeds. Hence, if a seeding mechanism would be operative, $AlCl_3$ would not be necessary to improve the sintered properties. Therefore, a seeding mechanism can be discarded for the enhancement of sintering spinel in the presence of $AlCl_3$.

Table 3
Properties of magnesium aluminate spinel sintered at 1550°C with 0.03 mol% of $AlCl_3$ added as a sintering aid to the partially "spinelized" powder obtained without any additive and fully "spinelized" powders obtained with 0.03 mol% $AlCl_3$ and 0.01 mol% AlF_3 respectively in the raw mix prior to calcination

Property	$AlCl_3$ "spinelized"	AlF_3 "spinelized"	Without "spinelizer"
Bulk density (g/cc)	3.27	3.20	3.40
Apparent porosity (%)	5.06	7.01	0.193
Water absorption (%)	1.90	2.18	0.057

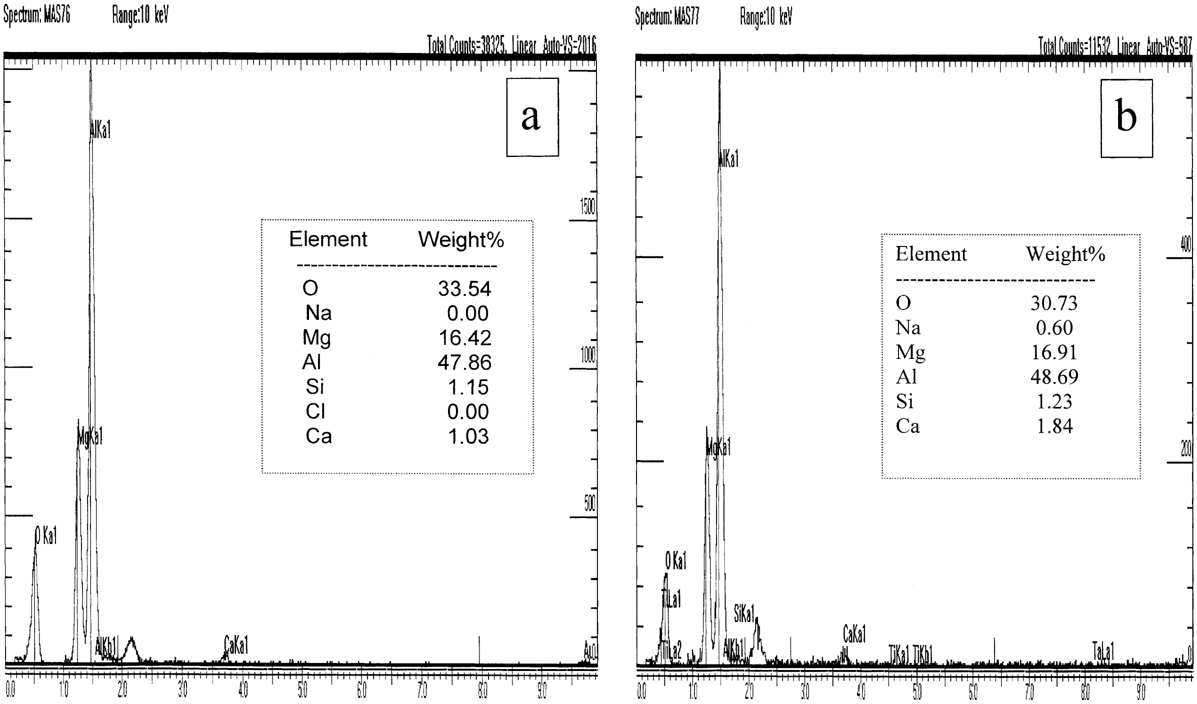
Another possible factor responsible for the densification of $MgAl_2O_4$ in the presence of $AlCl_3$ is liquid phase sintering where sintering aids generally act as flux during sintering and reduce the sintering temperature by forming low melting phases [17,21]. Recently, energy dispersive analysis with X-rays (EDAX) has emerged as a powerful tool for the detection of impurities. In order to identify the presence of any chloride containing material, $MgAl_2O_4$ spinel samples sintered at 1550°C for 1 h in the presence of 0% and 0.03 mol% $AlCl_3$ were subjected to EDAX. The EDAX (Fig. 6a and b) results clearly indicate the absence of chloride in the material. Therefore, liquid phase sintering may not occur in this case. Another interesting point to be noted based on the above mentioned EDAX results (Fig. 6) is the absence of Na after sintering in the case of $AlCl_3$ incorporated spinel (Fig. 6a) as compared to spinel without any additive (Fig. 6b). Probably, the presence of chloride may assist in the evaporation of Na_2O, which is one of the harmful impurities, by forming NaCl (melting point, 800°C; boiling point, 1465°C [22]) during sintering at above 1500°C. This may be an added advantage for using $AlCl_3$ as a sintering aid.

As there is no clear apparent relationship between the seeding effect or liquid phase sintering and improved sintered properties of $MgAl_2O_4$ spinel in the presence of $AlCl_3$, one could postulate regarding the possible role of moisture present during the sintering process. $AlCl_3$ is a more hygroscopic material in nature as compared to AlF_3. During its pyrohydrolysis, $AlCl_3$ will be converted into Al_2O_3 and HCl and Al_2O_3 contains surface hydroxyl groups and physisorbed moisture. According to Peri



(a) (b) (c)

Fig. 5. Scanning electron micrograph of sintered MAS at 1550°C for 1 h (a) fractured surface of MAS without any additive; (b) fractured surface of MAS in presence of 0.03 mol% $AlCl_3$; (c) fractured surface of MAS in presence of 0.03 mol% AlF_3.



Element	Weight%
O	33.54
Na	0.00
Mg	16.42
Al	47.86
Si	1.15
Cl	0.00
Ca	1.03

Element	Weight%
O	30.73
Na	0.60
Mg	16.91
Al	48.69
Si	1.23
Ca	1.84

Fig. 6. Energy dispersive analysis with X-rays of sintered MAS at 1550°C for 1 h in the presence of (a) 0.03 mol% $AlCl_3$; (b) without any additive.

[23,24], physisorbed water is driven away from the surface at 400°C, leaving a layer of hydroxyl groups. Removal of these hydroxyls is relatively easy as long as each OH^- has a neighbouring OH^- to condense with and to form water vapour. Monte Carlo simulations indicated that once the surface coverage decreases to 9.6%, the remaining hydroxyls are isolated. Further removal requires migration of hydroxyl groups to a new site. Because of the difficulty of removing an isolated OH^-, hydroxyl groups are still present at 1000°C where the sintering process is supposed to initiate. Thus the removal of moisture affects the mobility of ions in oxides by changing the defect concentration [25] resulting in enhanced diffusion. This may be a possible reason for the improvement in the sintering characteristics of $MgAl_2O_4$ spinels when doped with hygroscopic $AlCl_3$ as a sintering aid.

4. Conclusions

1. In a double stage firing process, $MgAl_2O_4$ spinel can be sintered to a bulk density of 3.40 g/cc, apparent porosity of 0.193% and water absorption of 0.057% using $AlCl_3$ as a sintering additive at a temperature of 1550°C.
2. $AlCl_3$ is effective in enhancing spinel formation during calcination and also acts as a sintering aid to improve sintered properties. Although, the conventional additive AlF_3 is capable of promoting spinel formation during calcination, it is not effective as a sintering aid. $AlCl_3$ is also capable of removing soda, one of the major impurities, during sintering of $MgAl_2O_4$ spinel.
3. $AlCl_3$ acts as a sintering aid only when the calcined powder contains free MgO and free Al_2O_3.
4. The hygroscopic nature of $AlCl_3$ is probably responsible for the formation of OH^- ions at the surface of the Al_2O_3 particles and the removal of these OH^- ions during the sintering process leads to an increase in defect concentration resulting in improved sintering.

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