Effect of MgCl\textsubscript{2} Addition on the Sintering Behavior of MgAl\textsubscript{2}O\textsubscript{4} Spinel and Formation of Nano-particles

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Abstract:
In this paper, the effect of MgCl\textsubscript{2} addition on the sintering behavior of MgAl\textsubscript{2}O\textsubscript{4} spinel produced via oxide mixture method was investigated. For this reason, the stoichiometric mixture of magnesite and calcined alumina as raw materials was calcined at 1100°C. The calcined mixture was milled, pressed and then, fired at 1300 and 1500°C after addition of various amounts of MgCl\textsubscript{2}. Besides, the physical properties, phase composition and microstructure of fired samples were investigated. The results showed that MgCl\textsubscript{2} addition has great effect on the densification and particle size of spinel. Besides, MgCl\textsubscript{2} addition increases the amount of spinel phase at all firing temperatures. Due to the decomposition of MgCl\textsubscript{2} and then formation of ultra-fine MgO particles, the nano-sized spinel is formed on the surface of the larger spinel particles.

Keywords: Sintering; Magnesium chloride; Spinel; Nano-particles; Phase composition

1. Introduction
Magnesium aluminate spinel (MgAl\textsubscript{2}O\textsubscript{4}) is a ternary oxide whose chemical formula is AB\textsubscript{2}O\textsubscript{4}, where A represent a divalent metal cation that normally occupies a tetrahedral site and B represents trivalent metal cations that normally occupy the octahedral sites of a cubic packed crystal [1 and 2]. Spinel is an important ceramic material, and possesses a unique combination of desirable properties such as high melting point (2135°C), good mechanical strength both at room temperature and elevated temperatures, high chemical inertness, low thermal expansion coefficient, and high thermal shock resistance. Hence, spinel is an excellent refractory material which is used in bottom and side walls of steel teeming ladles, transition and burning zones of cement rotary kilns, checker work of glass tank furnace regenerators, etc [3-7]. However, at the present time, the high cost of the sintered spinel and electro-fused spinel lowers the consumption of this refractory material. Conventionally, MgAl\textsubscript{2}O\textsubscript{4} spinel powders were prepared by solid-state reaction process using oxide MgO and Al\textsubscript{2}O\textsubscript{3} as starting materials. In the solid-state process, the mixture of MgO and Al\textsubscript{2}O\textsubscript{3} were usually calcined at temperatures as high as 1400–1600°C to ensure the phase formation. Sintering of such powders would be at extremely high temperatures (>1700°C) [8-11]. Formation of spinel from its constituent oxides is a counter diffusion process of Al\textsuperscript{3+} and Mg\textsuperscript{2+} ions and the reaction is associated with a volume expansion of 5% [11]. Reactant alumina with higher specific gravity converts to spinel with lower density results this expansion, which again does not allow the densification of formed spinel in the same firing. Hence a separate firing is required for whole densification of the formed spinel, enhancing the cost of

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production [3, 8-11]. Generally, the reaction between MgO and Al₂O₃ begins at about 900°C, but becomes noticeable only above 1400°C up to 1600°C [9 and 13]. Effects of different additives on the development of spinel were studied by a number of researchers [3, 11, 13-23]. Addition of salt vapors was found to enhance the spinel phase content. Besides, alkali fluorides addition leads to increase the crystal growth of formed spinel which can hinder the sintering process [14]. Kostic and et. al [15] reported that fluorine ion from AlF₃ or CaF₂ increases the solid-state reaction synthesis of magnesium aluminate spinel by increasing the cation vacancy. Addition of LiF was reported to decrease spinel formation temperature and increase spinel phase content [16]. Ganesh and coworkers [19] found AlCl₃ and AlF₃ are effective in enhancing spinel formation during calcination and also AlCl₃ acts as a sintering aid to improve sintered properties. Besides, the addition of mineralizers such as, V₂O₅, Y₂O₃, TiO₂ and B₂O₃ can help to formation of spinel to some extent [17 and 19]. Sarkar and Bannerjee found [20] that the addition of TiO₂ improved the density of alumina rich and stoichiometric spinels sintered at 1550 °C, but at higher sintering temperatures, higher amount of additive showed a deteriorating effect due to grain growth. Addition of Cr₂O₃ in spinel bodies is also available in the literature. Ju and co-workers [18] observed improved resistance in spinel bodies against thermal spalling and slag attack in presence of Cr₂O₃ and also reported that Cr₂O₃ makes solid solution with spinel phase. However, the use of these additives contaminates the product and restricts its application to low temperatures [11, 17, 19-21]. The object of the present work is to investigate the effect of MgCl₂ addition on the sintering behavior of stoichiometric spinel. For this reason, the stoichiometric mixture of magnesite and calcined alumina as raw materials was calcined at 1100°C. The calcined mixture was milled, pressed and then, fired at 1300 and 1500°C after addition of various amounts of MgCl₂. For this reason, physical properties, phase composition and microstructure of sintered products were studied.

2. Experimental procedure
2.1. Raw materials and composition

Calcined alumina (source of Al₂O₃) and highly pure local magnesite (source of MgO) were used for the preparation of spinel (MgAl₂O₄). The chemical compositions of these starting materials are given in Tab. I. The calcined alumina used was a product of Fiberona Co. (HTM 10, India). The magnesite used in this investigation [derived from Birjand regions (Iran)] was finely milled mineral magnesite [Mg(CO₃)] supplied by Arya Kani Sepahan Co. (Iran). Chemical analysis of the magnesite used shows that its purity is high and has a little amount of impurities like iron oxide and alkalis.

<table>
<thead>
<tr>
<th>Oxide (wt.%)</th>
<th>Raw material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnesite</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.96</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.2</td>
</tr>
<tr>
<td>MgO</td>
<td>46.91</td>
</tr>
<tr>
<td>Na₂O</td>
<td>Trace</td>
</tr>
<tr>
<td>CaO</td>
<td>1.44</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Trace</td>
</tr>
<tr>
<td>L.O.I</td>
<td>47.28</td>
</tr>
</tbody>
</table>

The specifications of raw materials used are shown in Tab. II. The Magnesium chloride (MgCl₂) used was a product of Kimia mavad Co. (Iran) which its specifications are
shown in Tab. III. Considering the Al$_2$O$_3$–MgO binary system phase diagram as well as the chemical composition of magnesite, detailed in Tab. 1, mixture of 71.67 wt. % magnesite and 28.33 wt. % calcined alumina was used. The MgCl$_2$ was added to the compositions in proportions of 0.5, 1, 2, 3, and 6 wt. %.

**Tab. II** The specifications of raw materials used

<table>
<thead>
<tr>
<th>Specification</th>
<th>Raw material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnesite</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.1</td>
</tr>
<tr>
<td>$D_{50}$ ($\mu$m)</td>
<td>2.6</td>
</tr>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**Tab. III** The specifications of magnesium chloride used

<table>
<thead>
<tr>
<th>Purity (%)</th>
<th>Melting Point (°C)</th>
<th>Solubility at water (20 °C)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;99</td>
<td>714</td>
<td>54.3 g/100 ml</td>
<td>2.32</td>
</tr>
</tbody>
</table>

### 2.2. Preparation of samples

The required proportions of the starting materials of each mix were dry blended together, and then calcined as loose powders in high alumina crucibles at 1100°C with 1 hr soaking time. Then, the calcined mixture was ground and homogenized in a laboratory planetary mill for 2 h with distilled water, using corundum balls as the grinding bodies. The size distribution of milled particles was analyzed by a laser particle diameter analyzer (Honeywell Microtrac X–100) after milling. The average particle size of the ground powder was around 2.39 $\mu$m. In order to make the MgCl$_2$ distribute evenly throughout the mixture, the MgCl$_2$ was dissolved in the hot water (80°C) and then was added to other raw materials in the ball mill. After being milled, the prepared mixtures were dried and then, were granulated. After that, the granulated powder was formed into briquettes under pressure of 800 kg/cm$^2$ and then, dried at 110°C. The firing of samples was carried out at 1300 and 1500 °C, with a soaking time of 3 h in an electric furnace.

### 2.3. Test methods

Bulk density and apparent porosity were measured according to ASTM C-373-88 standard. The XRD measurements were carried out with a D8ADVANCE, Bruker diffractometer with Cu K$_\alpha$, Ni-filtered radiation. The fracture surface of fired samples after gold coating was evaluated by field emission scanning electron microscope (FE-SEM), JEOL of model 7500 F.

### 3. Results and discussion

#### 3.1. The effect of MgCl$_2$ addition on the physical properties

The relation between bulk density and apparent porosity of prepared samples with different amounts of MgCl$_2$ as a function of firing temperature are shown in Figs. 1 and 2.

The results show that as the firing temperature is increased, the sintered properties of prepared samples are also found to increase. Composition without additive results in a very poor density on sintering at 1300°C, but this increases sharply with the increase in the sintering temperature (1500°C). On the other hand, the results show that the bulk density
enhances with increasing of MgCl₂ content and then, the apparent density decreases at all firing temperatures. Significant increase in density is observed at 1500°C (87%) and almost fully dense (96%) MgAl₂O₄ ceramics can be obtained at 1500°C in presence of 3 wt. % MgCl₂. At 1500°C, the bulk density of 3 and 6 wt. % MgCl₂ containing samples is almost same and the open porosity level is almost 4%. It is worth mentioning that 3 wt. % MgCl₂ is sufficient to sinter prepared samples with appreciable density. Therefore, MgCl₂ addition accelerates the sintering rate and grain growth. Hence, MgCl₂ is useful as a sintering aid for improvement of bulk density and apparent porosity.

![Graph](image1.png)

**Fig. 1.** The relation between bulk densities of prepared samples with different amounts of MgCl₂ as a function of firing temperature

![Graph](image2.png)

**Fig. 2.** The relation between apparent porosity of prepared samples with different amounts of MgCl₂ as a function of firing temperature

### 3.2. The effect of MgCl₂ addition on the phase composition

The XRD result of calcined sample at 1100 °C is shown in Fig. 3. With respect to this result, low amount of spinel phase is formed in the calcined sample at 1100 °C. On the other hand, the periclase (MgO) and corundum (Al₂O₃) phases are present in the calcined sample.
Magnesite converts to periclase phase with calcination at 1100°C. Then, periclase reacts with calcined alumina which leads to formation of spinel phase. Generally, the formation reaction of spinel begins at 900°C and completes at high temperature (≥ 1600°C) [9, 12]. Therefore, low amount of spinel phase can form in the calcined sample at 1100°C.

![Image of XRD result](image1)

**Fig. 3.** The XRD result of calcined product at 1100°C

▲: Spinel, ■: Periclase, ●: Corundum

The XRD results of prepared samples without and in presence of 6 wt.% MgCl₂ additive after firing at 1300 °C are shown in Fig. 4.

![Image of XRD result](image2)

**Fig. 4.** The XRD results of sintered products at 1300 °C without and in presence of 6 wt.% MgCl₂

▲: Spinel, ■: Periclase, ●: Corundum

The results show that all the compositions after firing at 1300°C contain phases such as corundum, periclase and spinel. The presence of corundum and periclase in the composition after firing at 1300°C indicates that the reaction between these oxides is not completed. On the other hand, the results show that the amount of spinel phase in the sintered samples is increased with addition of MgCl₂. Therefore, it can be concluded that the amount
of formed spinel at 1300°C depends on MgCl$_2$ content. The XRD results of prepared samples without and in presence of 6 wt.% MgCl$_2$ additive after firing at 1500°C are shown in Fig. 5.

**Fig. 5.** The XRD results of sintered products at 1500 °C without and in presence of 6 wt.% MgCl$_2$

▲: Spinel, ■: Periclase, ●: Corundum

With respect to these results, the high amount of spinel phase was found at all compositions. Besides, very low amount of remaining raw materials such as periclase and corundum exist in prepared samples without MgCl$_2$. Comparison between XRD results of Fig. 4 and Fig. 5 reveals that the amount of remaining raw materials is considerably decreased with increasing of firing temperature. On the other hand, the amount of the spinel phase is increased with increasing of firing temperature. This means that the complete solid state reactions in these compositions are mostly occurred after firing at 1500°C. The proportion of the spinel phase in the fired samples at different temperature was determined by quantitative XRD analysis. The results are plotted in Fig. 6 as a function of MgCl$_2$ amount and firing temperature.

**Fig. 6.** The effect of MgCl$_2$ addition on the spinel amount in the sintered samples at 1300 and 1500°C
As it can be seen from the results of Fig. 6, the amount of spinel phase is increased with the addition of MgCl$_2$ at all firing temperatures. With respect to these results, MgCl$_2$ addition has great effect on the amount of formed spinel in the fired samples at 1300°C. Addition of AlF$_3$ or CaF$_2$ was reported to increase the solid-state reaction synthesis of magnesium aluminate spinel by increasing the cation vacancy [19]. The same mechanism may also be operative for MgCl$_2$. For study of MgCl$_2$ effect on the spinel formation, the defect structure models were investigated. Generally, the dissolution of MgCl$_2$ in the spinel structure can produce cations vacancies which, lead to increasing of diffusion and then, further formation of spinel. On the other hand, with dissolution of MgCl$_2$ in the spinel structure, the spinel peaks can shift to higher angels. For further investigation, the replacement of spinel peak concerning to [311] plane was studied. In Figs. 7 and 8 the effect of MgCl$_2$ addition on the replacement of spinel peak concerning to [311] plane are shown after firing at different temperatures. Figs. 7 and 8 clearly show the spinel peak was not shifted to higher angles at different firing temperatures by MgCl$_2$ addition.

![Figure 7](image1.png)

**Fig. 7.** The effect of MgCl$_2$ addition on the replacement of spinel peak concerning to [311] plane after firing at 1300°C

![Figure 8](image2.png)

**Fig. 8.** The effect of MgCl$_2$ addition on the replacement of spinel peak concerning to [311] plane after firing at 1500°C

Therefore, MgCl$_2$ can’t dissolve in the structure and then, cations vacancies do not produce. On the other hand, LiF can enhance the densification characteristics of spinel products through liquid-phase sintering [19] and [22]. Hence, MgCl$_2$ like LiF can enhance the
amount of spinel phase through liquid-phase sintering. Probably, the reactions between the impurities like Na$_2$O, SiO$_2$, etc., in the raw materials and MgCl$_2$, leads to formation of some low melting phases such as; sodium chloride and sodium silico-chloride. Besides, MgCl$_2$ can be considered as seeds for spinel formation. Ganesh, Bhattacharjee and Saha [19] have also observed a similar influence of AlF$_3$ on spinel formation. The same mechanism also is reported for AlCl$_3$. One of the main advantages of AlCl$_3$ or AlF$_3$ as an additive is that during calcination both are pyrohydrolyzed into Al$_2$O$_3$ and gaseous HCl and HF, respectively [19]. Therefore, these mineralizers do not contaminate the MgAl$_2$O$_4$ spinel product. The same mechanism may also be operative for MgCl$_2$. This additive is pyro-hydrolyzed into MgO particles and gaseous HCl. Then, MgO particles react with Al$_2$O$_3$ to form spinel phase. Besides, this additive like AlF$_3$ and AlCl$_3$ does not contaminate the cement product. As there is no clear apparent relationship between the seeding effect or liquid phase sintering and improved sintered properties of MgAl$_2$O$_4$ spinel in the presence of MgCl$_2$, one could postulate regarding the possible role of moisture present during the sintering process. MgCl$_2$ is a hygroscopic material in nature. During its pyrohydrolysis, MgCl$_2$ will be converted into MgO and HCl and MgO contains surface hydroxyl groups and physisorbed moisture. Generally, the removal of moisture affects the mobility of ions in oxides by changing the defect concentration resulting in enhanced diffusion [24]. This may be a possible reason for the improvement in the sintering characteristics of MgAl$_2$O$_4$ spinels when doped with hygroscopic AlCl$_3$ as a sintering aid.

### 3.3. The effect of MgCl$_2$ addition on the microstructure

The microstructure of composition without MgCl$_2$ after firing at 1300°C is presented in Fig. 9.

![Fig. 9. SEM photomicrograph of composition without MgCl$_2$ after firing at 1300°C](image)

As it can be seen, the microstructure of composition without MgCl$_2$ is porous and contains the crystalline phases with different grain size. According to XRD results of Fig. 4, the present phases in the composition without MgCl$_2$ after firing at 1300°C contain periclase, corundum and spinel that linked together via sintering process. The corundum presents a hexagonal morphology while periclase and spinel phases are seen as aggregates with some cluster of cubic shape crystals. On the other hand, the micron-sized large pores were observed in the sintered bodies. Considering that these pores have a size comparable to the average grain size (1.1 μm), they will be difficult to eliminate by the normal sintering mechanisms (grain-boundary diffusion or lattice diffusion) and are removable through abnormal grain growth during further densification. The origin of these large defects in the sintered materials
may be explained from the viewpoint of the compaction homogeneity of particles in the green bodies. Fig. 10 demonstrates the microstructure of composition containing 6 wt. % MgCl$_2$ after firing at 1300°C.

![Fig. 10. SEM photomicrograph of composition containing 6 wt.% MgCl$_2$ after firing at 1300°C](image)

With microstructural evaluation, one can see that the addition of MgCl$_2$ can lead to formation of higher cubic spinel in the composition which fired at 1300°C. Besides, as can be seen from Fig. 10, the ultra-fine cubic grains are formed when the MgCl$_2$ introduces into composition. According to the EDS analysis, these cubic grains were spinel phase. Therefore, the nano-spinel is formed with addition of MgCl$_2$, so that the grain size distribution of the formed spinel is in the range of about 60–90 nm. The microstructure of composition without MgCl$_2$ additive after firing at 1500°C is presented in Fig. 11.

![Fig. 11. SEM photomicrograph of composition without MgCl$_2$ after firing at 1500°C](image)

With comparison between microstructure of fired samples at 1300 °C with fired sample at 1500 °C, one can see that firing temperature caused a drastic change in the particle size and morphology of microstructure. So that, continuing grain growth and the homogeneous microstructure is observed as the sintering temperature increases. Besides, the exaggerated grain growth is observed for fired samples at 1500 °C so that the well-crystallized grains of spinel are formed. Therefore, at 1500 °C the grain growth during further densification sintering process occurs, first in the solid state and later in the presence of a liquid phase. The different morphologies are obtained. Generally some grains exhibit a plate
like shape with poorly defined edges. Also, well defined cubic and rounded grains are observed. On the other hand, the well-crystallized spinel connected with each other, indicating that the spinel synthesized using this method was of high purity. Fig. 12 demonstrates the microstructure of composition containing 6 wt. % MgCl₂ after firing at 1500°C.

![Fig. 12. SEM photomicrograph of composition containing 6 wt.% MgCl₂ after firing at 1500°C](image)

It appears that the microstructure of the sample containing 6 wt. % MgCl₂ is homogeneous with rounded and well defined direct-bonded spinel-spinel grains. With comparison between microstructure of fired samples at 1500 °C without MgCl₂ and containing 6 wt. % MgCl₂, one can see that the average grain size of spinel grains decreases with addition of MgCl₂ so that; the specimen containing 6 wt. % MgCl₂ has an average grain size of 0.8 μm. With microstructural evaluation, one can see that the addition of MgCl₂ can lead to formation of nano-particles on the surface of larger grains as shown in Fig. 13. With respect to EDX results, these nano-particles are in the spinel phase.

![Fig. 13. SEM photomicrograph of nano-particles on the surface of larger grains in composition containing 6 wt.% MgCl₂ after firing at 1500°C](image)

It is known that, additives like AlF₃ accelerate the facile generation of Al₂O₃ from its precursors which in turn results in a spinel formation at relatively lower calcination temperatures [19]. Therefore, one can conclude that MgCl₂ like AlF₃ can produce MgO as nano-particles. The use of MgCl₂ as water soluble additive leads to proper distribution of
Mg$^{2+}$ ions in the composition. Therefore, the nano-MgO active particles can form on the surface of particles in the composition. Then, reaction between these nano-particles with Al$_2$O$_3$ can lead to formation of nano-spinel particles in the composition.

4. Conclusions

In this paper, the stoichiometric mixture of magnesite and calcined alumina was calcined at 1100°C and then, the effect of MgCl$_2$ addition on the formation of spinel and sintering behavior of samples after firing at high temperatures was investigated. The results showed that the bulk density enhances with increasing of MgCl$_2$ content and then, the apparent density decreases at all firing temperatures. Besides, significant increase in density is observed at 1500 °C and almost fully dense MgAl$_2$O$_4$ ceramics can be obtained at 1500 °C in presence of 3 wt. % MgCl$_2$. The results showed that the amount of spinel phase is increased with the addition of MgCl$_2$ at all firing temperatures. MgCl$_2$ can enhance the amount of spinel phase through liquid-phase sintering. On the other hand, the removal of surface hydroxyl groups during the pyro-hydrolysis of MgCl$_2$ affects the mobility of ions in oxides by changing the defect concentration resulting in enhanced diffusion and then, the improvement in the sintering characteristics of MgAl$_2$O$_4$ spinels. The microstructural evaluation showed that the average grain size of spinel grains decreases with addition of MgCl$_2$. On the other hand, the addition of MgCl$_2$ leads to formation of nano-particles on the surface of larger grains. The MgCl$_2$ is pyrohydrolyzed into nano-MgO particles and gaseous HCl. Then, nano-spinel particles are formed on the surface of larger particles as a result of reaction of MgO with Al$_2$O$_3$.

5. References


Садржај: У овом раду је испитиван утицај додатка MgCl₂ на синтеровање спинела MgAl₂O₄ добијеног методом мешања оксида. Из тог разлога, стехиометријска смеша почетних прахова магнезијума и алумине је калцинисана на 1100°C. Калцинисана смеша је млевена, пресована и синтерована на 1300 и 1500°C након додатка различитих садржаја MgCl₂. Проучавани су фазни састав, микроструктура и физичка својства синтерованих узорака. Резултати показују да додатак MgCl₂ има велики утицај на густину и величину честица спинела. Поред тога, додатак MgCl₂ повећава количину спинелне фазе на свим температурама синтеровања. Услед разлагања MgCl₂ и формирања ультра- финих честица MgO, нано-честице спинела се формирају на површини већих честица спинела.

Кључне речи: синтеровање; магнезијум хлорид; спинел; нано-честице; фазни састав