

Formation of magnesium spinel in the presence of LiCl

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The formation of magnesium spinel through a solid state reaction was studied. The synthesis was produced by mixing reactant powders in different proportions and after thermal treatments at 950°C from 1 h to several days. The effect of LiCl on the kinetics of spinel formation was analysed. The mono-charged Li⁺ ion produces a deficient alumina and magnesia structure that accelerates the diffusion of Mg²⁺ and Al³⁺ into the respective oxides. The formation of spinel occurs into alumina particles. Transport through the gaseous phase of lithium and magnesium chlorides enhances the kinetics of production of magnesium aluminate. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Magnesium aluminate spinel (MgAl₂O₄) is an excellent refractory oxide of special technological importance as a structural ceramic. Its physical, chemical and thermal properties are useful at normal and elevated temperatures. It melts congruently at 2135°C [1], shows high resistance to attack by most of the acids and alkalis and has low electrical losses. Due to these desirable properties, it has a wide range of applications in structural, chemical, optical and electrical industries [2]. Studies on magnesium aluminate spinel have indicated that this material has superior swelling resistance compared to most metals and ceramics during fission neutron irradiation. Because of this behavior, spinel is considered to be a prime candidate insulator for fusion reactor applications [3].

The conventional ceramic preparation technique of complex oxide spinels is based on high-temperature solid state synthesis from simple oxide and/or hydroxide mixtures. Powdery spinel is produced by a solid-state reaction at temperatures in the range of 1450–1750°C. The reaction between aluminum oxide and magnesium oxide is a diffusion-controlled process, which depends mainly on the temperature and particle size of the initial powders. Diffusion is sufficiently fast above temperatures of 1500–1800°C [4]. The formation of Mg-Al spinel from a mixture of magnesia and alumina is accompanied by a large volume expansion, theoretically 8% [5].

An alternative method to synthesize a shaped spinel-bearing body was proposed, through the oxidation of solid Mg-Al₂O₃ precursor. The oxidation of Mg to magnesia is accompanied by a reduction in the solid volume, while the formation of spinel from the reaction of magnesia and alumina results in an increase of the solid volume. Consequently, the conversion of a dense Mg-Al₂O₃ precursor into a dense MgAl₂O₄ body should result in a small net volume change [6].

In order to obtain the spinel with high reactivity and chemical homogeneity, several techniques through co-precipitation (800–1000°C) [7], spray-pyrolysis (700–900°C) [8], sol-gel (400–1200°C) [9] and freeze-drying have been investigated. Recently, the mechanochemical route was proposed as one of the alternative methods for spinel synthesis [10].

The interaction between transition alumina, lithium and magnesium was observed in the Saffil fibers used in the metal matrix composites (MMCs). Those fibers consist of polycrystalline δ -Al₂O₃ preform, infiltrated with liquid metals like magnesium-lithium alloys. From the thermodynamic point of view, the system Al₂O₃-Mg-Li is unstable. The reaction leading to the formation of MgO, Li₂O, lithium aluminates and magnesium spinels may occur having a negative influence on the properties of the fibers [11]. The δ -Al₂O₃ decomposition and gradual formation of a spinel compound, accompanied by lithium and magnesium penetration into the Saffil fiber, was observed. However, no remarkable

interaction between δ - Al_2O_3 and liquid magnesium had been observed in the study of the interaction of fibers with pure magnesium [11].

The aim of this work is to attain a faster and lower temperature process for the formation of magnesium spinel, analyzing the mechanism of this reaction, and to determine the effect of the presence of LiCl on the kinetics of the spinel formation reaction.

2. Experimental

The following raw materials were used for preparing the reactant powders: Aluminum oxide from ceramic source, magnesium oxide chrom. ads. anal., and lithium chloride anal. reagent.

The starting powders were weighed and added to the aluminum oxide in different proportions to obtain different concentrations, after that they were mixed with a Y-shaped mixer for 1 h.

The samples were placed in quartz crucibles and maintained at 950°C in air. The thermal treatments were carried out into an open electric furnace, for periods from 1 h to several days.

In those mixtures which contained magnesium chloride, the heatings were fulfilled into a sealed reactor with an air purge, in order to remove the developing hydrochloric acid. The solid residues were analysed by SEM: scanning-electron microscopy, EDS: energy-dispersive spectroscopy and XRD: X-ray diffraction.

3. Results and discussion

The characteristics of alumina, magnesia and lithium chloride used in the present work are shown in Fig. 1.

The alumina powder has a particle size below $100\ \mu\text{m}$ with grains of about $2\ \mu\text{m}$, being a mixture of two phases: the metaestable θ -alumina and the stable α -phase. As can be seen from the diffraction pattern (Fig. 1a), the α -phase is present as the major one. After three days of heating at 950°C no change was observed between the Intensity Ratio of the two phases, meaning that the proportion between them was maintained. These results are indicating that there was not a phase transformation under this experimental condition. The morphology of the particles after heating remains the same as the starting one.

On the other hand, the magnesia powder was decomposed at 300°C for 72 h and MgO was obtained in the periclase phase, see XRD pattern in Fig. 1b. The SEM photograph shows particles composed by fine plates which did not experience morphological changes after heating for 2 days at 950°C .

Finally, the LiCl was dried for four days at 80°C , resulting in a mixture of the anhydrous and the hydrated phases of this compound. As can be seen in Fig. 1c, LiCl particles of about $200\ \mu\text{m}$ in size are formed by fine grains in the order of $10\ \mu\text{m}$ diameter and they appear to be covered by a coating.

Another compound like $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, was also used in a few experiments with the purpose of clarifying certain behaviors.

- Effect on the $\theta \rightarrow \alpha$ transformation.

Aluminium oxide (Al_2O_3) has a unique stable crystalline phase, named corundum or α -phase. Other intermediate phases of Al_2O_3 (γ -, δ - and θ - Al_2O_3), known

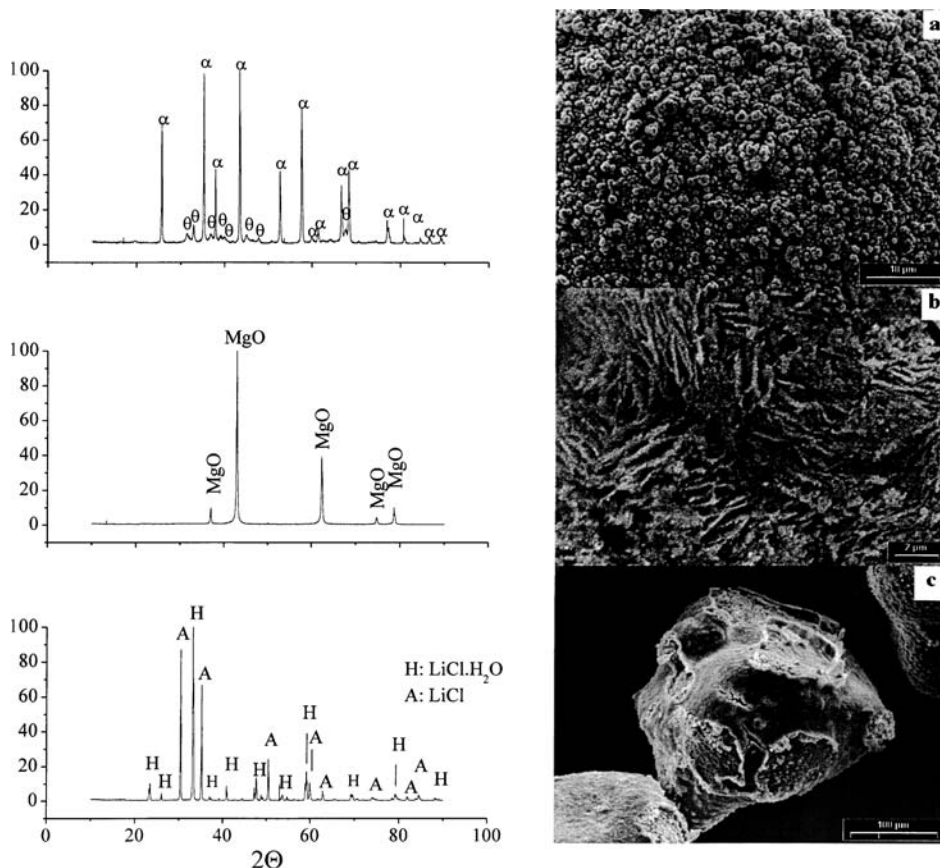


Figure 1 XRD patterns and SEM images of the starting samples: (a) Al_2O_3 , (b) MgO and (c) LiCl.

as transition aluminas, are metastable and structurally similar phases. The transformation of transition aluminas to α -phase involves a dehydration process. Several factors, like the presence of impurities and the heating atmosphere, affect the kinetics and the starting temperature of the transformation from the metastable θ -alumina to the stable α -alumina [12]. In the present work, the effect of different contents of MgO after heating in air at 950°C during different times was analyzed. As it is shown in Table I, the ratio between the maximum intensity of the two phases is slightly modified by the presence of magnesia after seven days of heating. As the strongest peak of magnesia is very close to the most intense peak of α -alumina, and could be introduced as an error in the measurement of the peak intensities, Table I shows the intensity ratio of a phase corresponding to the position $2\theta = 35.166^\circ$ (90%) and 57.571° (80%) for the α -alumina and $2\theta = 32.806^\circ$ (100%) for the θ -alumina. These results confirm a weak effect of magnesia on the metastable transformation of the alumina. It was also observed that the ratios do not change from 72 h to seven days and that is why 72 h was the longest heating time in the following experiments.

Although the effect on the transformation was not strong, a change in the morphology of the starting magnesia was observed, see Fig. 2a and b. As can be seen in the images, the plate-like structure of magnesia was preserved, but there was an important grain growth after heat treatment. Besides, 4 to 15 at% of Al was detected by EDS on magnesia surface, but magnesium was not noticed on the alumina particles. The presence of Al

on the MgO particles indicates that Al^{3+} diffuses into magnesia easier than Mg^{2+} into alumina, i.e., Al^{3+} ions are the fastest diffusing species which may be attributed primarily to the small ionic radius of Al^{3+} in comparison to Mg^{2+} [13].

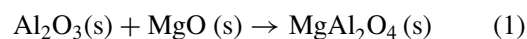
The effect of the presence of LiCl at different concentrations after 72 h of heating at 950°C was also analyzed. In Table I the ratios between peak intensities of α -alumina and θ -alumina are shown. At very low proportions of LiCl, the phase transformation is weakly enhanced by its presence after prolonged treatment, but any other phase has not been detected by XRD, indicating that, if it is formed, its volume concentration is below 2 wt%, which is the detection limit for almost all mixtures, by the powder diffraction method. For proportions above 1 wt% of LiCl, the θ -phase disappeared and the LiAl_5O_8 was formed.

These results are the starting point for comparison with further systems in the present study.

Solid State Reaction for Aluminates Formation.

- Mixtures: Xw% Al_2O_3 + Yw% MgO:

The global reaction for the formation of magnesium aluminate through a solid-solid reaction can be expressed as follows:



The standard free energy change ΔG° of this reaction is -24.145 kJ at 25°C and -26.676 kJ at

TABLE I Ratio between the absolute peak intensities of the θ - Al_2O_3 and α - Al_2O_3 , in different mixtures and for several periods of heating

	Initial		48 h				7 days	
	17 wt% MgO + 83 wt% Al_2O_3	35 wt% MgO + 65 wt% Al_2O_3	17 wt% MgO + 83 wt% Al_2O_3	35 wt% MgO + 65 wt% Al_2O_3	0.5 wt% LiCl + 99.5 wt% Al_2O_3	0.7 wt% LiCl + 99.3 wt% Al_2O_3	17wt% MgO + 83 wt% Al_2O_3	35 wt% MgO + 65 wt% Al_2O_3
$\frac{I_{\theta(200)}}{I_{\alpha(113)}}$	0.17	0.17	0.14	0.13	0.14	0.11	0.13	0.13
$\frac{I_{\theta(200)}}{I_{\alpha(104)}}$	0.17	0.20	0.14	0.14	–	–	0.14	0.14
$\frac{I_{\theta(200)}}{I_{\alpha(116)}}$	0.20	0.20	0.17	0.17	–	–	0.17	0.17

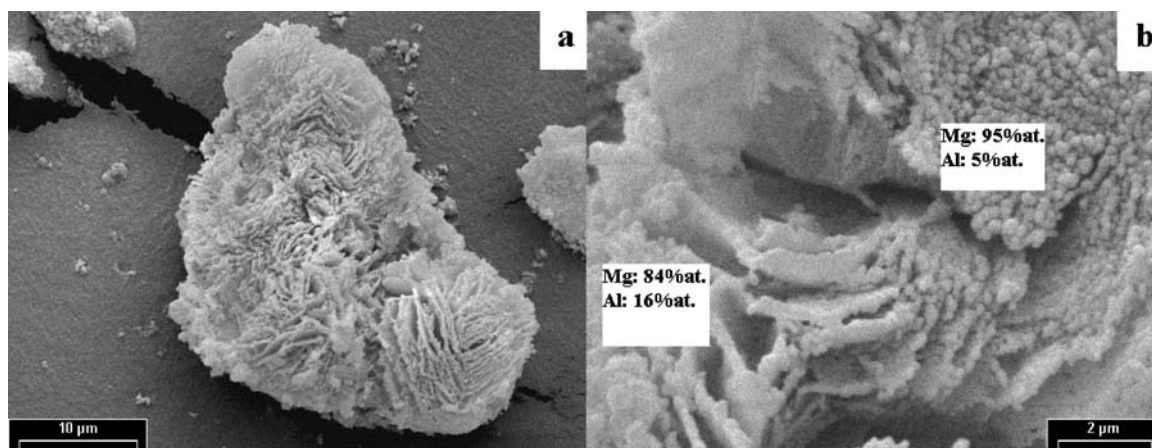


Figure 2 Morphology of MgO 35 wt% + Al_2O_3 65 wt% mixtures, after heating at 950°C for 3 days.

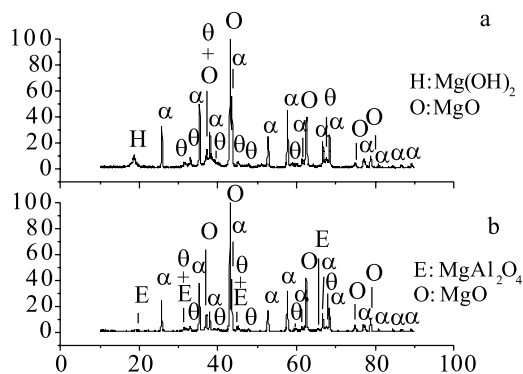


Figure 3 XRD patterns of: (a) Starting mixture of MgO 35 wt% + Al₂O₃ 65 wt%. (b) Same sample after heating at 950°C for two weeks.

950°C. This thermodynamical property indicates that magnesium aluminate formation is probable by the solid reaction of alumina with magnesia from room temperature.

Although the stoichiometric relation for the formation of the magnesium spinel in accordance with reaction (1), is 28 wt% MgO, a small amount of magnesium aluminate was obtained after heating the mixture 35 wt% MgO + 65 wt% Al₂O₃ at 950°C for two weeks.

As can be seen in Fig. 3, all the spinel peaks are superimposed with the θ -alumina, except those at $2\theta = 19$ and 65° .

Intensities of spinel peaks are less than 5% with respect to the most intense peak in the pattern, meaning that the amount of magnesium spinel is very small after holding the sample a long time at high temperature. Consequently, the kinetics of this solid-solid reaction is too slow to produce aluminate efficiently.

Furthermore, the morphology of magnesia and alumina particles is well defined, after the heat treatment. The plate like shape of magnesia particles is the same as the starting sample, but a more detailed examination at a higher magnification reveals crystal growth, with the appearance of fine grains at the external plate edges, as it is shown in Fig. 2. Likewise, the alumina particles are very similar to the starting sample. The EDS analysis made on the alumina particles detected only Al, but those obtained from the magnesia particles demonstrated the presence of Mg and Al on their surfaces. See Fig. 2b.

These results are suggesting that it is easier for the Al³⁺ ions to incorporate into the magnesia particles than to the Mg²⁺ ions to diffuse into the alumina. The high proportion of Al, between 5 and 16 at.%, detected on magnesia particles and the small amount of spinel showed by the XRD pattern, manifest that the formation of MgAl₂O₄ does not occur in magnesia particles.

- Mixtures: X wt% Al₂O₃ + Y wt% MgO + Z wt% LiCl:

There are two stable phases of lithium aluminate in the temperature range used in this work, LiAlO₂ and LiAl₅O₈. The two species may be formed depending on the reaction conditions and the precursors [14–18].

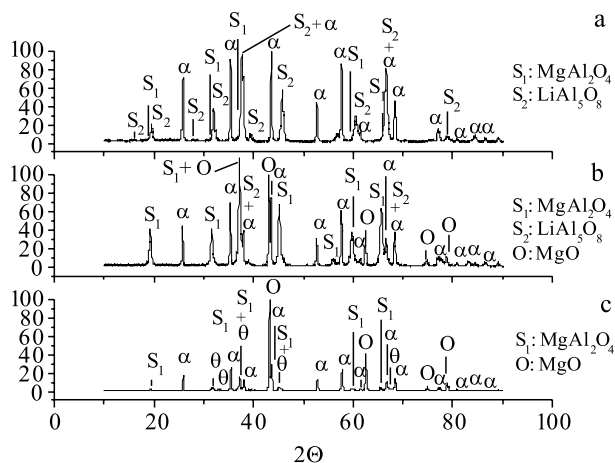
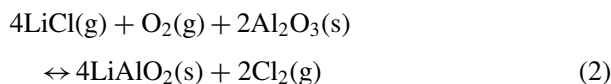


Figure 4 XRD patterns of different mixtures after thermal treatment at 950°C for 72 h: (a) LiCl 15 wt% + MgO 5 wt% + Al₂O₃ 80 wt%, (b) LiCl 5 wt% + MgO 17 wt% + Al₂O₃ 78 wt% and (c) LiCl 0.5 wt% + MgO 35 wt% + Al₂O₃ 64.5 wt%.

The ΔG° for the formation of LiAlO₂ following this reaction:



$\Delta G^\circ(25^\circ\text{C}): -472 \text{ kJ}$ and $\Delta G^\circ(950^\circ\text{C}): -40 \text{ kJ}$ [19]

The stoichiometry requires 14 wt% LiCl.

The comparison of ΔG° between reactions (1) and (2) shows a less negative value of ΔG° for the reaction (1), which is demonstrating that, from thermodynamics considerations, the formation of lithium aluminate is more favorable than the magnesium spinel in the working temperature range.

As can be seen in Fig. 4, after heating mixtures of alumina, magnesia and lithium chloride at 950°C for 72 h, the formation of LiAl₅O₈ predominates when there is a high content of LiCl (15 wt%) with low magnesia proportions and when the amount of LiCl decreases (5%), the formation of lithium aluminate diminishes. For amounts of LiCl less than 5 wt%, α -alumina and magnesium aluminate were only detected. In Fig. 4, it is also shown that when the amount of MgO is increased the amount of magnesium aluminate obtained increases too. In Table II, it is expressed the ratio between the relative intensities of three well-defined peaks of magnesium aluminate with respect to α -alumina, in mixtures with high content of MgO and different proportions of

TABLE II Ratio between the absolute peak intensities of the α -Al₂O₃ and MgAl₂O₄. Effect of the LiCl concentration, when the mixture is heated at 950°C for 72 h

LiCl wt%	0.3 wt%	0.5 wt%	0.7 wt%	1 wt%	5 wt%	10 wt%	15 wt%
$I_{\alpha(113)}$	12	7	7	5	1	1	0.2
$I_{\text{MgAl}_2\text{O}_4(440)}$							
$I_{\alpha(113)}$	13	11	13	9	1	1	0.4
$I_{\text{MgAl}_2\text{O}_4(511)}$							
$I_{\alpha(113)}$	18	13	14	11	2	1	0.4
$I_{\text{MgAl}_2\text{O}_4(111)}$							

TABLE III Ratio between the absolute peak intensities of the α -Al₂O₃ and MgAl₂O₄. Effect of the LiCl concentration after different times of heating at 950°C

$I_{\alpha(113)}$ 1 MgAl ₂ O ₄₍₄₄₀₎	0.3 wt%	0.5 wt%	0.7 wt%	1 wt%	5 wt%	10 wt%
	LiCl	LiCl	LiCl	LiCl	LiCl	LiCl
3 days	12	7	7	5	1	1
6 days	–	–	–	4	1	1
18 days	6	5	7	–	–	–

LiCl. The reduction of intensity ratios with increasing the LiCl content is showing the major formation of aluminate which indicates a promoting effect of LiCl on the synthesis of magnesium spinel. The formation of lithium aluminate in this mixture was not observed. In Table III, it is possible to follow the evolution of values of the intensity ratio with heating time. It can be seen that an increase of the holding time at high temperature does not produce a considerable increase in the magnesium spinel formation. Similar results were obtained in mixtures with 17% of MgO.

From the analysis of the whole set of experiments, the mixture with 73%Al₂O₃ + 17%MgO + 10%LiCl treated at 950°C for three days, apparently represents the best condition for the synthesis of a significant amount of magnesium spinel.

As can be observed in Fig. 5, the formation of aluminates produces a well-defined change on the surface of particles. After treatment at 950°C for 72 h, there are two types of morphologies in all the mixtures used. In Fig. 5a and b it is presented the one related with particles

of magnesia and in Fig. 5c and d the one related with alumina. A higher content of LiCl produces an increase of the magnesia grain size, from 0.1 μ m with 0.7 wt% to 1 μ m with 10 wt% of LiCl. The well-faceted cubic shape crystallites and their marked agglomeration are indicating the high ionic mobility at this temperature. The alumina particles show that the grain size has not changed noticeably but, at low MgO and high LiCl contents a condensate covered the particles like an amorphous coating.

EDS analysis, showed that Mg and Al were present in the sample, but no Cl was detected, which is indicating that only the cations are diffusing into the particles. The average amounts of Al and Mg detected in 1 μ m³ on magnesia surfaces were 30 at.% Al and 70 at.% Mg which is less than the amount needed for the formation of aluminate. On the other hand, the elemental quantification on alumina particles reveals the following average values at high MgO and low LiCl: 43 at.%Mg and 55 at.%Al, which approximates better to the composition of aluminates but indicating a mixture of this with alumina, while at low MgO and at high LiCl, the values are 85 at.% Al and 15at.% Mg and it is too low for the formation of aluminates but in this sample lithium aluminate and alumina were solely detected. It is quite possible that the Mg was incorporated in both of these phases as a solid solution.

- Mixture: X wt%Al₂O₃ + P wt%MgCl₂

In order to verify the role of Cl⁻ in the present synthesis, mixtures with different amounts of alumina and

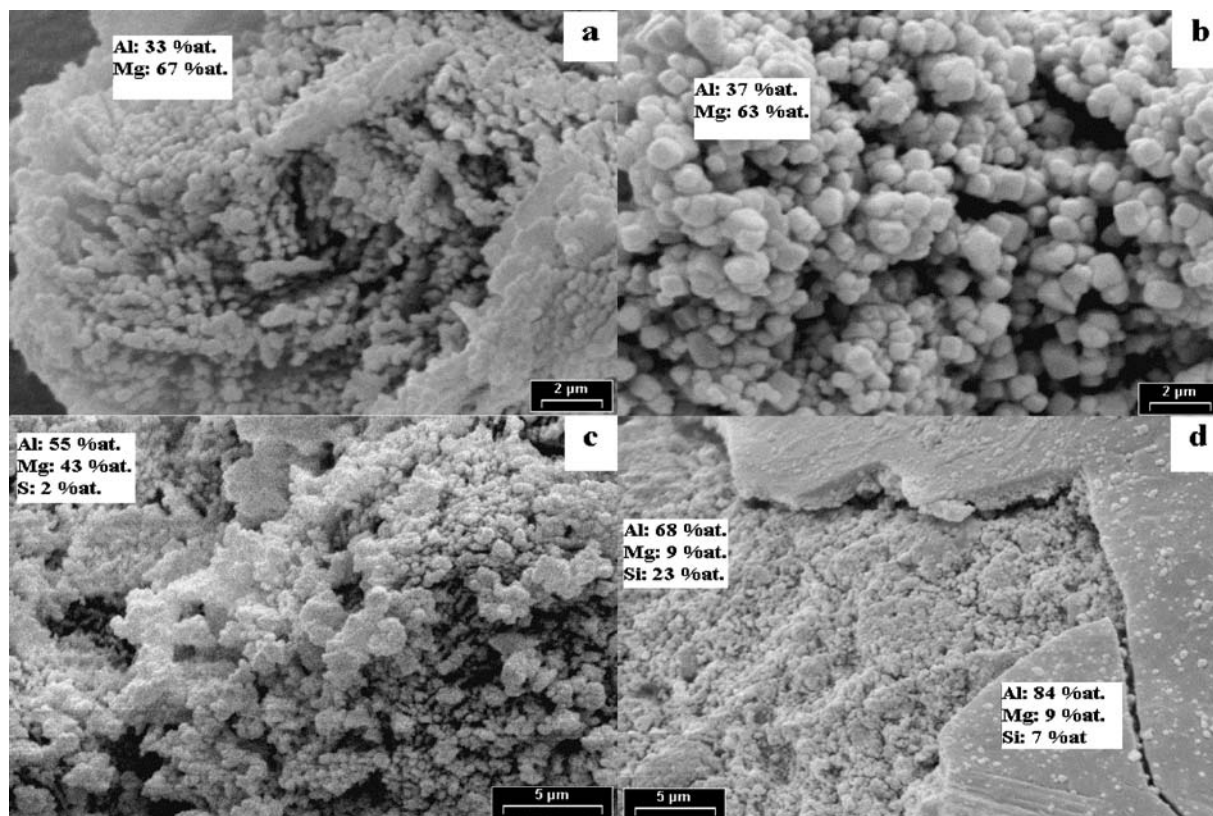
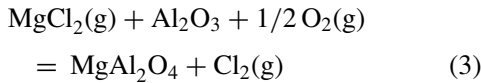


Figure 5 SEM images of the morphology of different mixtures after heating at 950°C for 72 h: (a) LiCl 0.7 wt% + MgO 35 wt% + Al₂O₃ 64.3 wt%, (b) LiCl 10 wt% + MgO 35 wt% + Al₂O₃ 55 wt%, (c) LiCl 15 wt% + MgO 5 wt% + Al₂O₃ 80 wt%, and (d) LiCl 0.7 wt% + MgO 35 wt% + Al₂O₃ 64.3 wt%.

TABLE IV Ratio between the absolute peak intensities of the α -Al₂O₃ and MgAl₂O₄. Effect of the Cl⁻ ion on the spinel formation

950°C 72 h	41 wt% MgCl ₂ ·6H ₂ O + 59 wt% Al ₂ O ₃	17 wt% MgO + 5 wt% LiCl + 78 wt% Al ₂ O ₃	35 wt% MgO + 15 wt% LiCl + 50 wt% Al ₂ O ₃
I _{α(113)} I MgAl ₂ O ₄₍₄₄₀₎	3	1	0.2
I _{α(113)} I MgAl ₂ O ₄₍₅₁₁₎	6	2	0.4
I _{α(113)} I MgAl ₂ O ₄₍₁₁₁₎	5	2	0.5
No reacted Al ₂ O ₃ moles per 100 g of sample	0.376	0.705	0.323

magnesium chloride were prepared. The magnesium chloride used was an hexahydrated substance which losses its six water molecules above 230°C. Besides, the decomposition of MgCl₂ in MgO is thermodynamically favorable from 500°C and, consequently, the final species that reacts with alumina is the oxide. The mixture with 83% MgCl₂·6H₂O is above the stoichiometry of the following reaction:



The XRD pattern shows the presence of magnesium spinel and magnesium oxide and the alumina of the starting sample seems to have completely reacted. The appearance of the magnesium oxide demonstrates the decomposition of magnesium chloride at 950°C, so the MgCl₂ acts as a precursor that provides a better contact between MgO and Al₂O₃, through the vapor phase transportation. Additional studies with a non-stoichiometric mixture containing 41 wt% MgCl₂·6H₂O was analyzed. In Table IV, the intensity ratios between alumina and magnesium spinel, of the last mixture after heating for 72 h at 950°C, are presented. It is compared with other mixtures where the MgCl₂ may be formed from the reaction between LiCl and MgO. Although the excess of alumina for the MgCl₂ mixture is approximately the excess for the 35 wt% MgO mixture but less than that with 17 wt% MgO, the intensity ratios for the previous experiments are smaller than those corresponding to the MgCl₂ samples. This result gives evidence that there is another phenomena which is contributing to a better diffusion of magnesium into alumina for the spinel formation, and it may be due to the incorporation of Li⁺ into the alumina, generating vacancies.

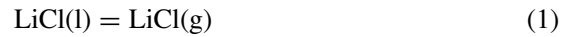
Mechanism of magnesia spinel formation.

Further experiments were planned for elucidating the path by which the synthesis of spinel occurs. Two new mixtures were prepared and treated at 950°C for 72 h: Al₂O₃ + (17 and 35 wt%)LiCl and MgO + 36 wt%LiCl. In the first mixture, the lithium aluminate was formed with remarkable changes of the particle shapes. Then the magnesia powder was incorporated to reach the next composition: 45 wt%.Al₂O₃ + 35 wt%.MgO+ 20 wt%LiCl. This mixture was treated

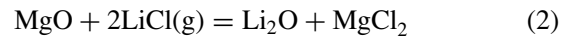
at 950°C for 24, 48 and 72 h, and it was observed that the ratio between the peaks of lithium spinel and α -alumina was always the same. It means that no reaction between lithium spinel and magnesia particles was detected. It is apparent that the route by which the magnesium spinel was formed was not through the incorporation of Mg⁺² into the lithium aluminate.

The second binary mixture (MgO + 36%LiCl) was also treated at 950°C for 72 h. As can be seen in Fig. 6, the crystal growth of magnesia particles and the formation of well-faceted crystal with cubic habit is significant. XRD proves that the two phases of starting LiCl had disappeared and the only product detected is MgO. Then the alumina powder was incorporated to reach the next composition: 45 wt%.Al₂O₃ + 35 wt%.MgO + 20 wt%LiCl. After heating for 10 days at 950°C, an increase of the magnesia spinel peaks and the lithium aluminate peaks was observed. The presence of lithium aluminate is indicating the transportation of Li⁺ ion from magnesia to alumina particles, while the Cl⁻ ion has left the sample, as demonstrated by EDS analysis, and Li⁺ was incorporated into magnesia as a solid solution. These results suggest that the lithium spinel is preferentially formed in the alumina particles, while the long time required for the formation of small amounts of magnesium aluminate indicates that the magnesium spinel can not be generated until the Li⁺ ions penetrate the alumina. Moreover, the slow formation of spinel may be due to the the absence of Cl⁻ in the sample.

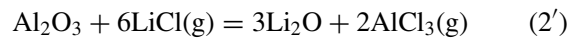
According to the previous results the following global mechanism is proposed:



$$\Delta G^0 = 47 \text{ kJ (950°C)}$$



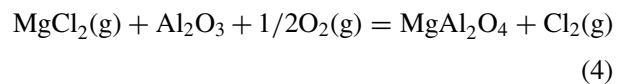
$$\Delta G^0 = 114 \text{ kJ (950°C)}$$



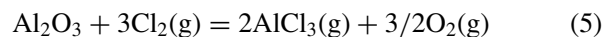
$$\Delta G^0 = 563 \text{ kJ (950°C)}$$



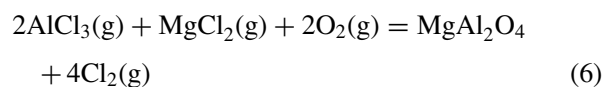
$$\Delta G^0 = 42 \text{ kJ (950°C)}$$



$$\Delta G^0 = -155 \text{ kJ (950°C)}$$



$$\Delta G^0 = 248 \text{ kJ (950°C)}$$



$$\Delta G^0 = -325 \text{ kJ (950°C)}$$



$$\Delta G^0 = -18 \text{ kJ (950°C)}$$

Reaction (1) ensures homogeneity in the distribution of LiCl on the surfaces of magnesia and alumina

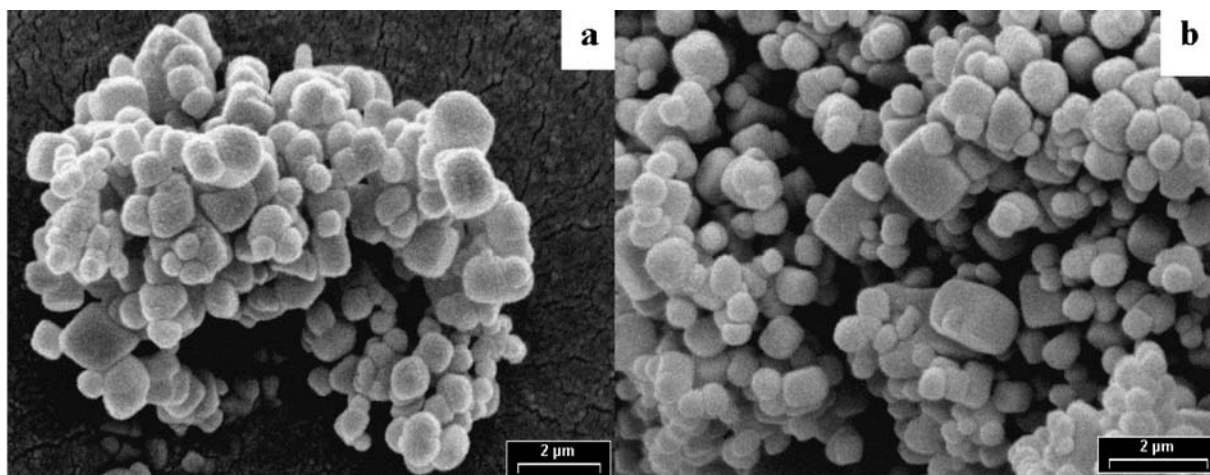


Figure 6 Images of the morphology of LiCl 36 wt% + MgO 64 wt% mixtures after treatment at 950°C for 72 h.

particles. Reaction (2) even thermodynamically unfavorable, may be produced because reaction (4) consumes the MgCl_2 product. The formation of Li_2O may be interpreted as the dissolution of Li^+ into magnesia particles, replacing Mg^+ in a solid solution. This replacement generates a vacancy that enhances the incorporation of Al^{3+} into the magnesia structure, which was detected by EDS with an increase of the Al amount on the MgO grains like was shown in Fig. 2. Reaction (3) is shifted to the volatilization of MgCl_2 by reaction (4) which is thermodynamically favorable. The gaseous MgCl_2 attacks homogeneously the alumina in the presence of air. The formation of magnesium spinel produces gaseous chlorine that may react with alumina giving $\text{AlCl}_3(\text{g})$, which may interact with $\text{MgCl}_2(\text{g})$ in air, also producing the magnesium spinel with a displacement of reaction (5) by reaction (6). Nevertheless, a remarkable increase of the alumina grain growth was not observed, then reaction (4) is kinetically more favorable than reaction (6) in this synthesis. The $\text{MgCl}_2(\text{g})$ would react with the $\text{O}_2(\text{g})$ of air with the corresponding recrystallization of MgO on the magnesia surfaces, producing an important growth of faceted grains with the habit of magnesia.

4. Conclusions

A low temperature solid state method for the formation of magnesium aluminate was developed. The presence of mono charged anions like Li^+ and Cl^- , enhances the kinetics of the solid state reaction. The reaction is kinetically favorable in the mixture of oxides which were mixed in ratios 7 wt% higher than the stoichiometry.

The diffusion of aluminum into magnesia is enhanced by Li^+ . The dissolution of Li^+ creates vacancies which improve the atomic mobility and produce crystal growth with less energy consumption.

The effect on the kinetics of the $\theta \rightarrow \alpha$ transformation confirms the Li^+ incorporation in the alumina lattice, generating vacancies that facilitate the dehydration of the transition alumina towards the stable corundum. Although the θ -phase had disappeared at the beginning

of the spinel formation, the reaction occurs practically with the alumina in the α -phase, and continues with heating.

The creation of a defective alumina structure with the mono charged cation dissolution, leads to the penetration of Mg^{2+} into the alumina structure generating a topochemical process for the formation of spinel.

Although the structure of lithium spinel is an open ion net, which may allow the diffusion of aluminum enhancing the formation of magnesium aluminate [20]; the present results indicate that the mechanism of magnesium spinel formation is through the dissolution of Mg^+ into alumina particles and further reaccommodation of the structure. The kinetics of this process are enhanced by the transport through gaseous phase of volatile chlorides (MgCl_2 and LiCl) that improves the interaction among reactants.

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