EFFECT OF Fe ON SINTERING OF Al₂O₃-MgO-Fe₂O₃ SPINEL

O.V. Kharissova, J.A. Aguilar, U. Ortiz

ABSTRACT

The influence of Fe on the microstructure of Al₂O₃-MgO-Fe₂O₃ spinel is described in this work. Heating a mixture of initial oxides in an electric furnace at 1400º C for 15 hrs produced the spinel. A ternary diagram for concentration ranges: Al₂O₃ (5-75 mol%), MgO (10-80 mol%), and Fe₂O₃ (3-70 mol%) summarize the constitution of this spinel. Amount, composition and weight ratios of each phase were determined by X-rays powder diffraction. Microstructure of specimens was characterized by scanning electronic microscopy and X-ray spectrometry. Distribution, size, shape of phases and pores were examined. Hardness measurements of spinel completed this study.

INTRODUCTION

The magnesia-alumina spinel (MgAl₂O₄) has a cubic crystal structure that shows similarities and differences to those of both, magnesia (MgO) and alumina (Al₂O₃). MgO and spinel have cubic close-packed arrays of oxides, in contrast to Al₂O₃ which has a distorted hexagonal close packed array of oxide ions. The Al³⁺ ions occupy octahedral sites in both Al₂O₃ and spinel, while the Mg²⁺ ions are octahedral in MgO but tetrahedral in MgAl₂O₄ [1].

The (MgAl₂O₄), that has a melting point of 2135°C, is the only intermediate compound in the phase diagram of the system MgO-Al₂O₃. Spinel forms two eutectics, one of them at 45 wt% of magnesia with a melting point of 2030°C; the other eutectic at 97 wt% of alumina with a melting point of 1925°C [1]. As it was described above, this structure is determined by the space configuration of relative large oxygen ions, with trivalent and bivalent cations between them. Due to the relative size of the oxygen, it is possible to have certain disorder without major changes in the lattice. This situation gives a wide range of compositions for the spinel Al₂O₃*MgO. In this spinel, the MgO/Al₂O₃ ratio is 28.2 wt% to 71.8 wt%, but it varies within wide limits. Most magnesia-alumina spinel compositions have approximately the same lattice constant [2]: 0.8nm, up to about 0.85nm. All oxygen ions in the lattice are equivalent, forming a close packed structure; thus X rays analysis of the spinel structure does not reveal any differentiation of the oxygen ion arrangement in the lattice.

The spinel is a solid solution that behaves according to the interaction of the present species, quantitatively considered by thermodynamics trough the activity. The interesting role of the iron is that it bears two charges, it could be either a bivalent (+2) or trivalent (+3) ion, and therefore it could take either of the sites of the magnesium or the alumina. It is clear that the properties would be also different and dependent of the chosen site. The presence of this third element changes the phase diagram, according to the new activity of the species.
The aim of this work focuses on a summary of the results of tests conducted for producing magnesia-alumina spinel at 1400°C and to see how iron influences on the sintering. One idea is that iron makes easier to produce the spinel with properties good enough to be compared to the spinel produced at higher temperature from magnesia and alumina only. However this asseveration depends of the valence of the iron and the location that it would take in the lattice.

Diffusion tests between MgO and Fe₂O₃ to form MgFe₂O₄ spinel, shown that the two interfaces moved in the ratio of 1:2.7, close to the ideal value of 1:3. It was established earlier [3] that Al³⁺ diffusion in MgO at high temperatures is related with the presence of vacancies. While other researcher [3] showed that the amount of vacancies, created by dissolution of Al³⁺ in MgO, is directly proportional to Al³⁺ concentration in the range 1560-1900°C.

**SPINEL PRODUCTION**

From thermodynamic considerations, magnesia and alumina should react to form MgAl₂O₄ spinel. But it is necessary to heat the MgO/Al₂O₃ powder mixture at high temperatures, above 1200°C, for having a reaction at an appreciable rate. If the reaction were taking place in a solid phase, the first stage of reaction would be the formation of MgAl₂O₄ nuclei. This nucleation is difficult because of the differences shown in the structure of reactants and products, and the large amount of structural reorganization that is involved in forming the product.

MgAl₂O₄ spinel is usually produced in two ways: by smelting production and by sintering production. Smelting production allows having liquid materials in an intimate mixture that ensures that the diffusion between species gives a stable structure, in this case the spinel. In the sintering process, the temperatures are lower than in the smelting process, and the spinel is achieved just on the external part of the grains. The spinel is formed in the neck between the grains where the driving force for diffusion is stronger. In this case, it is common to add other elements for reducing the processing temperatures, but this also affects the properties of the final product.

To reduce sintering temperature of spinel, ZnO and SiO₂ are used as impurities. When Zn²⁺ is present in Al₂O₃ matrix, the interstitial vacancies of Al³⁺ or oxygen can be increased. Fe₂O₃ can also reduce sintering temperature. For example, if simple crystals of Al₂O₃ have 0.5 %wt. of Fe₂O₃ at 1500 °C, spinel Fe (Fe₁-xAlₓ)₂O₄ begins to grow [4]. Understanding the nature of the spinel lattice is possible to select the appropriate additive that gives both, low temperature processing and allows a smelter sintering.

**EXPERIMENTAL PROCEDURE**

A series of samples with different composition in the system MgO-Al₂O₃-Fe₂O₃ was prepared from precursors Fe₂O₃, MgO, and Al₂O₃. MgO was heated to 800°C before use due to its hygroscopic properties.

Weighted mixtures {Fe₂O₃: MgO: Al₂O₃=(3-70 mol%): (10-80 mol%): (5-73 mol%)} were wet milled and pressed in the crucible and heated at 1400°C for 15 hrs. Then, the samples were studied by X-rays diffraction. The color of the samples depends on percentage of iron introduced: from white to dark brown.
RESULTS AND DISCUSSION

In the process of spinel synthesis from oxides-precursors, the bands of oxides should be broken in order to allow migration of atoms in considerable distances (in the atomic scale). Such ions as Mg$^{2+}$ in MgO and Al$^{3+}$ in Al$_2$O$_3$ are usually determined as fixed in their appropriate cell sites, so it is difficult for them to move to empty sites. Only at high temperatures, such ions have sufficient thermal energy, which permits them to leave their normal sites and diffuse through the crystal. For obtaining such energy, it is necessary to increase the temperature or to introduce a melting additive for decreasing the sintering temperature.

In this work, we have used Fe$_2$O$_3$ as an additive for optimizing spinel production by means of decreasing the processing temperature and increase the reaction rate. The behavior of different concentrations of Fe$^{3+}$ ions in MgO-Al$_2$O$_3$ system was studied in detail. The results are presented in the Figure 1 and Table 1, which shows a presence of different phases in the system MgO-Al$_2$O$_3$-Fe$_2$O$_3$.

![Figure 1](image_url)

Figure 1. Ternary equilibrium diagram for the magnesia-alumina-hematite system showing the chosen compositions and the phases found.

MgO, Al$_2$O$_3$, MgAl$_2$O$_4$  
MgAl$_2$O$_4$, Mg(Al$_{0.91}$Fe$_{0.09}$)$_2$O$_4$  
MgO, Mg(Al,Fe)$_2$O$_4$  
Mg(Al,Fe)$_2$O$_4$

The first samples were prepared without iron and gave about 39-48% of MgAl$_2$O$_4$ spinel, depending on the mixture composition. When Fe$_2$O$_3$ (3 mol%) was added, spinel percentage increased to 64%. Further increase of iron content to 5% increased the spinel formation to 76% and decreased periclase (MgO) and corundum (Al$_2$O$_3$). This means that the presence of iron allows producing the spinel, although not all of MgO reacted with Al$_2$O$_3$ (Figures 2 and 3). Presence of less than 9 mol% of iron allows spinel sintering, but iron ions do not enter in its structure. They form AlFeO$_3$ and do not change its oxidation state to Fe$^{2+}$. In the same conditions, MgAl$_2$O$_4$, MgO, Al$_2$O$_3$, and AlFeO$_3$ are present.

As a result of the increase of Fe content to 10mol%, two types of spinel are formed: MgAl$_2$O$_4$ and Mg(Al$_{0.91}$Fe$_{0.09}$)$_2$O$_4$ (Figure 4 and 5).
Table 1. Phases in the system MgO-Al$_2$O$_3$-Fe$_2$O$_3$. The second row corresponds to mixture composition (mol%) and the third one corresponds to the percentage of the encountered phases for each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>7</th>
<th>33</th>
<th>28</th>
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<td>50</td>
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<td>50</td>
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<tr>
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<td>30</td>
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<tr>
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<td>5</td>
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<td>Al$_2$O$_3$</td>
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<tr>
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<td>76</td>
<td>85</td>
<td>53</td>
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<tr>
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<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg(Al,Fe)$_2$O$_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Mg(Al$<em>{0.91}$Fe$</em>{0.09}$)$_2$O$_4$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>47</td>
<td>0</td>
</tr>
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</table>

Figure 2. X rays diffraction pattern of the sample number 12 (5 mol% of Fe$_2$O$_3$).

MgO reacted completely; meaning that Fe$^{3+}$ entry in MgAl$_2$O$_4$ structure. At 20–45 mol% of Fe$_2$O$_3$, Fe$^{3+}$ ions react completely and form Mg(Al,Fe)$_2$O$_4$ as a single phase.

Free hematite was found at compositions quite above this range (above 60%), but looking at the X-rays diffraction patterns carefully we found that the stable phase is maghemite ($\text{Fe}^{III}_{2}\text{O}_3$).

Although the nucleation is complicated in the conditions of spinel sintering, a series of successive steps, including spinel phase growth, can take place. The presence of Fe$_2$O$_3$ allows obtaining spinel with or without Fe$^{3+}$ ions at temperatures lower than 1400°C. Presence of Fe$^{3+}$ ions can change spinel surface due to the introduction of them into its structure.

MgAl$_2$O$_4$ nucleation is accompanied by reorganization of oxide ions in the site of potential nuclei together with exchange of Mg$^{2+}$ and Al$^{3+}$ ions through the interfaces between MgO y Al$_2$O$_3$ particles.

It was possible to measure Rockwell 15T hardness only in the samples with more than 10 mol% of Fe$_2$O$_3$ (Table 2).
Figure 3. A SEM image of the sample number 12 (5 mol% of Fe$_2$O$_3$ showing MgO.

Figure 4. X - rays diffraction pattern of the sample number 33 (10 mol% of Fe$_2$O$_3$).

Table 2. Rockwell Hardness, 15T

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Fe$_2$O$_3$ mol%</th>
<th>MgO mol%</th>
<th>Hardness Rockwell,15T</th>
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<td>40</td>
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<tr>
<td>21</td>
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<td>30</td>
<td>36±6</td>
</tr>
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CONCLUSIONS

In this work, it was demonstrated that the production of magnesia-alumina spinel at 1400°C is possible when hematite is added to the magnesia-alumina mixture. The presence of iron produces compounds such as maghemite and magnesioferrite. Above 50 mol% of hematite the spinel mixture does not show any increase in iron compounds and hematite is left out of the solid solution. An important issue is that the iron is used as an impurity, or better as an additive for decreasing the temperature processing of the spinel. Iron increase the rate of spinel production above 10 mol% and densification of samples was possible. Rockwell 15T hardness measured was around 45. Corundum and periclase phases have a hard influence over the measured hardness.

ACKNOWLEDGMENTS

Authors express their gratitude to CONACYT (Mexican Council for Science and Technology) and PAICYT (University of Nuevo León, Research Program for Science and Technology) for its financial support.

REFERENCES