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Low Temperature Synthesis of Spinel Powders by Mechanical Grinding

E. Yalamaç[1], S. Akkurt[2] and M. Çiftçioğlu[3]

[1] Materials Science and Engineering Program, Izmir Institute of Technology, 35430 Izmir, Turkey

[2] Mechanical Engineering Department, Izmir Institute of Technology, 35430 Izmir, Turkey

[3] Chemical Engineering Department, Izmir Institute of Technology, 35430 Izmir, Turkey

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Abstract. Low temperature synthesis of spinel powder via intense mechanical grinding was performed. A dramatic decrease in the synthesis temperatures of ground powders was achieved. We were able to produce partially crystallized spinel at room temperature via a 110 minute grinding. Characterization of the synthesized powders was performed using SEM, XRD and DTA. Each stage of synthesis was analyzed using these techniques. Mixtures of $Mg(OH)_2$ and $Al(OH)_3$ were used for synthesis. Temperatures as low as 800 ^oC were able to produce bumps in the XRD patterns of ground powders at the 2θ angles for spinel crystals..

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) provides a combination of desirable physical, chemical and thermal properties, both at room temperature and elevated temperatures [1]. It melts congruently at 2135 °C, which 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 industry. It is used as a refractory lining in steel-making furnaces, transition and burning zones of cement rotary kilns [2].

Synthesis and fabrication of spinel $MgAl_2O_4$ is known for a long time. A number of techniques such as, conventional solid-state-reaction (SSR) [3], co-pecipitation route [4], and gelation-precipitation process [5] have been extensively employed. In addition to these methods, mechanochemical route is the recently used method for low temperature spinel synthesis [6, 7].

Intense grinding activates ceramic powders [7]. This procedure enhances the development of solid-state processes. The mechanical energy produces structural imperfections in the powder particles during grinding, and this effect increases the reactivity of ground materials. Grinding, which is based on impact and friction, further increases the chemical reaction rates via particle size reduction which in turn increases the specific surface area [8].

In this study, intense mechanical grinding was employed as a tool to lower the synthesis temperature of $MgAl_2O_4$ spinel.

Experimental

Gibbsite ($Al(OH)_3$) (MERCK) and magnesium hydroxide ($Mg(OH)_2$) (SIGMA) were used as raw materials that were mixed in stoichiometric proportions to attain spinel composition. 6 g of mixture was weighed and placed in a planetary ball mill (Fritsch Pulverisette-6). Six sintered corundum (Ø: 20 mm) balls were used as the grinding media in a 250 ml sintered corundum mill container. The mixtures were ground at 600 rpm for varying durations from 5 to 230 minutes. The equipment was paused after every 15 minutes of operation in order to avoid excessive heating. In the second set of experiments, 10 g of sample was ground for 60 minutes in the same grinding conditions, subdivided

into 1g samples which were heated at varying temperatures (600-1400 ^{o}C). The soak time was 2 hours and the heating rate was 5 ^{o}C/min.
X-Ray Diffraction (XRD) was employed to analyse the present phases and crystallinity of the ground and calcined mixtures (Philips X'pert Pro, XRD). DTA analysis was carried out in order to investigate thermal behaviour of the mixtures (Shimadzu DTA-50, Japan). The morphology and particle size of the mixtures were observed by scanning electron microscope (Philips XL-30S FEG, SEM).

Results and Discussion

XRD patterns of mixtures, which were ground at different grinding times, are shown in Figure 1. Intensities of raw materials decrease with increased grinding time and amorphization of the starting materials occurs at around 50 minutes. After 110 min of grinding, new phases of spinel and corundum were observed in the XRD pattern. Stronger peaks for corundum were observed with increasing grinding times because of wearing of sintered corundum pot and the grinding media. 230 min grinding resulted in a severe contamination of mixture by corundum from the pot and stronger corundum peaks overshadowed the spinel phase.

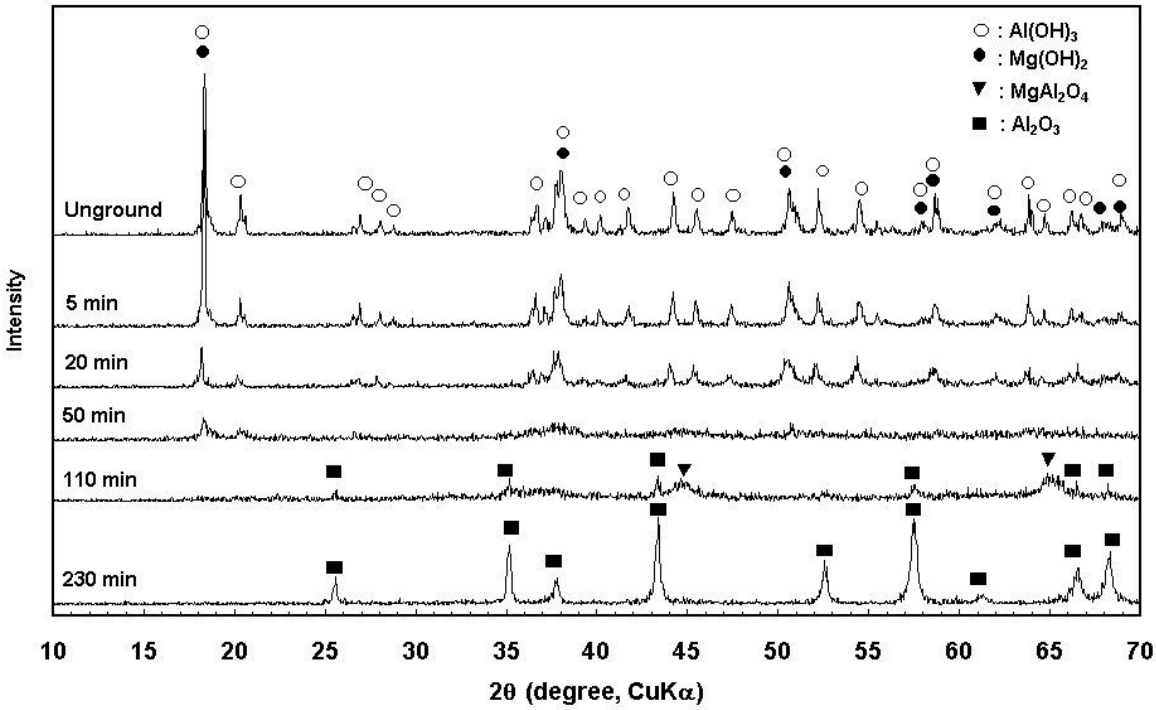


Figure 1. XRD patterns of the mixtures ground for various durations.

DTA analysis was also performed on the same samples. Results shown in Fig. 2 supported the findings of XRD analysis. Loss of structurally bound water from Al and Mg hydroxides was detected at 300 and 390 ^{o}C, respectively. These temperatures slightly decreased on increasing grinding times. The endothermic peak intensities also decreased on further grinding. After 230 minutes, there was no peak on the DTA chart.

Fig. 3 shows the XRD patterns of the 60 min ground mixtures, which were heat treated at different temperatures. The peaks of the raw materials did not disappear completely after 60 min of grinding since the amount of starting raw materials of 60 min ground sample (10 g) was much higher than that of the previously 50 min ground sample (4 g) which could reach complete amorphization.

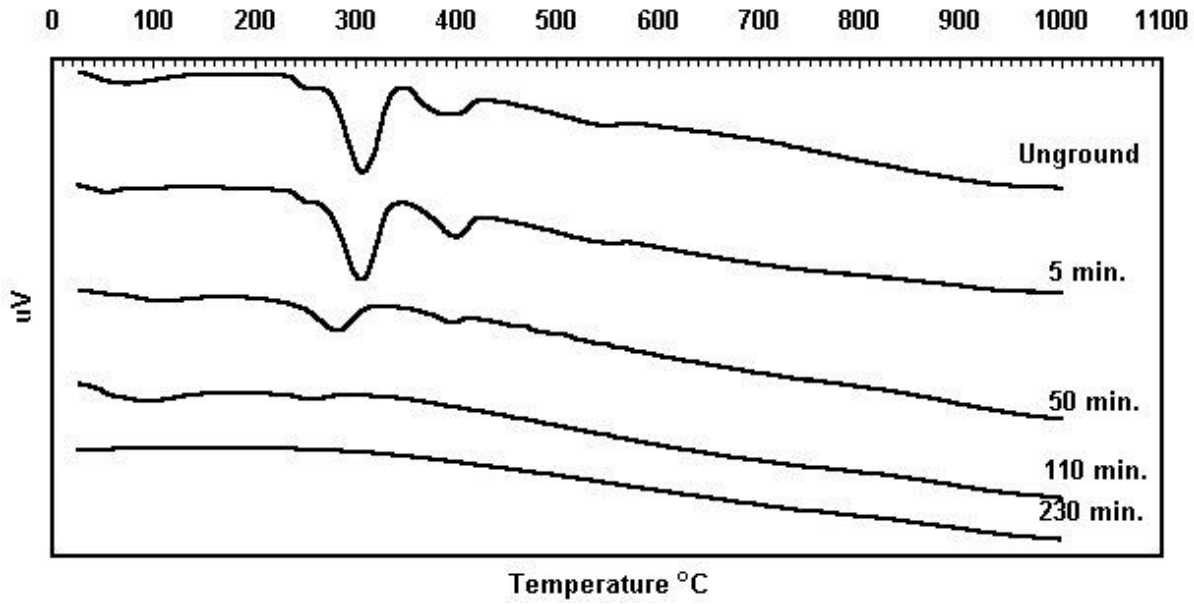


Figure 2. DTA analysis of ground mixtures.

However, when the mixture was heated at 600 °C, the original peaks of $Mg(OH)_2$ and $Al(OH)_3$ disappeared. When the calcination temperature went up to 800°C, the bump for periclase phase (MgO) was seen in the pattern in addition to the spinel bumps (Fig. 3). Further heating led to the disappearance of the periclase phase upon reaction with alumina, and the subsequent formation of spinel at 1000 °C. At 1200 °C and 1400 °C, spinel peak intensities became even higher than that of 1000 °C.

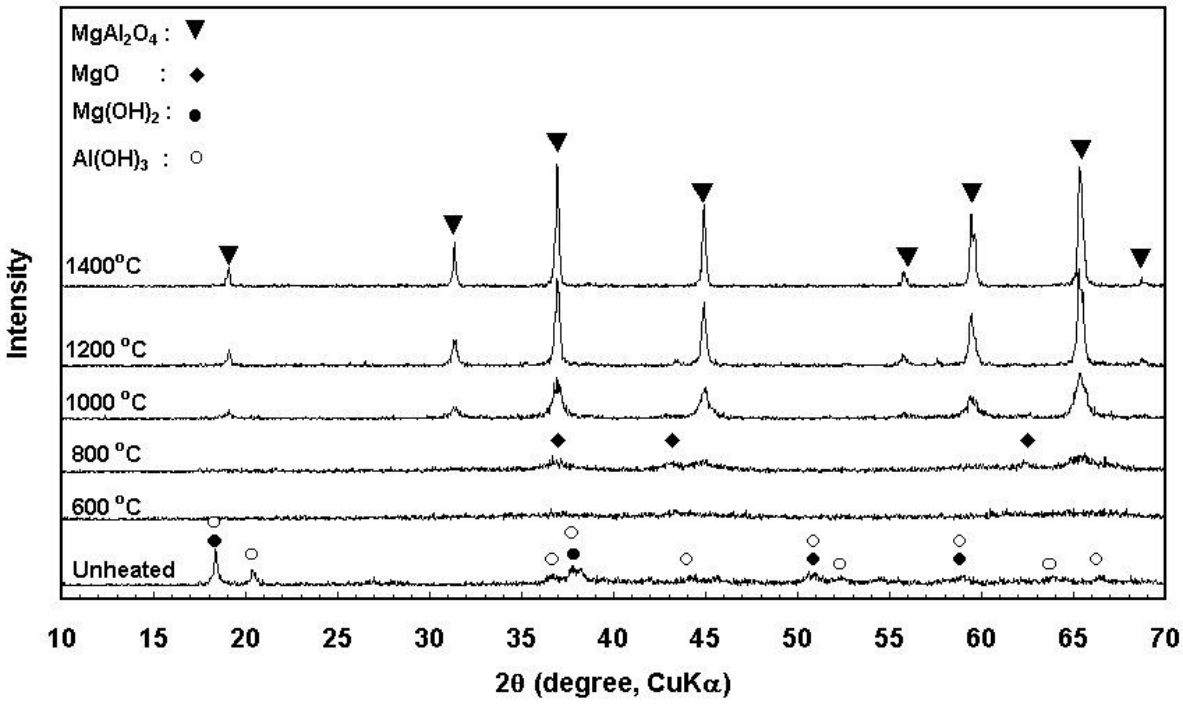
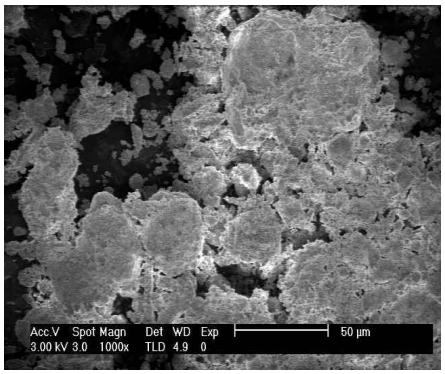


Figure 3. XRD patterns of the 60 min ground mixtures calcined at different temperatures.

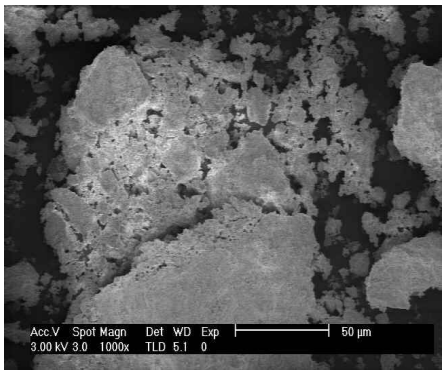
Secondary electron images of selected powder samples are shown in Figure 4. Significant particle size reduction was achieved by 5 min grinding (Fig 4-b). Further reduction occurred at 50 and 110 min grindings except that they contained agglomerates of fine particles.

Conclusions

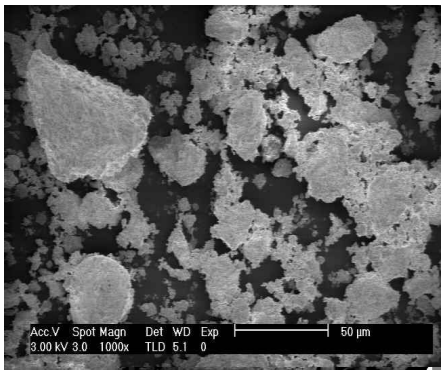
Synthesis of spinel powder was achieved at low temperature. Partial growth of spinel crystals in XRD patterns were detected after 110 minutes of grinding without heating. Heating of samples ground for 60 minutes produced spinel crystals at temperatures as low as 800 ^{o}C. Grinding media contamination problem was observed after excessive grinding durations. It was found that the amount of charge to the mill was an important factor in achieving amorphization within shorter grinding times. Further study is planned to investigate the effects of milling parameters on synthesis. Other crystals like cordierite and α-alumina will also be investigated.



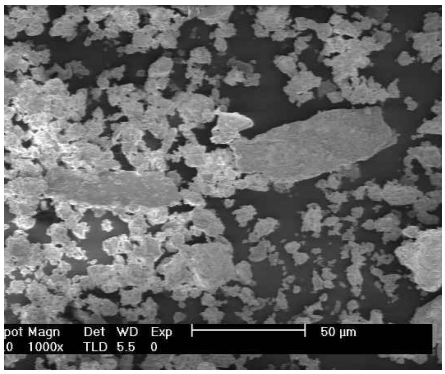
(a) Unground powder mixture



(b) After 5 minutes of grinding



(c) After 50 minutes of grinding



(d) After 110 minutes of grinding

Figure 4. SEM micrographs of powder specimens ground at 600 rpm.

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