Self-Propagating High-Temperature Synthesis of Magnesium Aluminate Spinel Using Mg–Al Alloy

Yi-kai Wang, Xiao Xie, and Chen-guang Zhu*

ABSTRACT: In this study, magnesium aluminate spinel (MgAl₂O₄) was synthesized by a self-propagating high-temperature synthesis method using Mg–Al alloy with a Mg/Al mass ratio of 50:50 as raw material. Synthesized MgAl₂O₄ was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, UV–vis diffuse reflectance spectroscopy, photoluminescence, and thermogravimetric differential scanning calorimetry techniques. The results show that synthesized products are of high purity and excellent crystallinity. However, the particle size is not uniform and there is obvious agglomeration. The crystallite size of spinel phase is calculated to be 37.78 nm. In the UV band, the synthesized MgAl₂O₄ has a certain absorption capacity, and the extrapolated band gap is 4.02 eV. The synthesis mechanism was studied, and continued rupture and growth of the oxidation layer is thought to be responsible for grain refinement.

1. INTRODUCTION

Due to their excellent thermal and chemical stability and high mechanical strength, spinel type oxides AB₂O₄ (where A and B represent two different cations of comparable ionic radius) are widely used in catalysis, ceramics, magnetic materials, humidity sensors, photoluminescent materials, and so on.¹–⁷ The abundance and low cost of aluminum and magnesium as precursors of MgAl₂O₄ compared to other elements make MgAl₂O₄ more widely used.⁸ MgAl₂O₄ usually is synthesized from MgO and Al₂O₃ by a direct solid-state reaction.⁹ Nevertheless, Mg₂Al₁₇O₃₄ generated from MgO and Al₂O₃ is accompanied by a volume expansion of about 8%. This is due to the molar volume difference between the reactants and products.¹⁰ A double firing process was proposed to solve this problem.⁹ However, owing to high costs of the process, a variety of alternative simple methods have been proposed such as combustion synthesis,¹¹–¹³ sol–gel,¹⁴,¹⁵ microwave-assisted combustion route,¹⁶ co-precipitation method,¹⁷ and so on. Among these processes, combustion synthesis, also known as self-propagating high-temperature synthesis (SHS), is an easy, fast, and cost-effective method for synthesizing composites.¹⁸

The SHS of Mg₂Al₁₇O₃₄ usually uses Al₂O₃/Mg or MgO/Al as a raw material.¹⁹–²¹ As a result, the particle size of synthesized MgAl₂O₄ is influenced by the raw material. Mg₂Al₁₇O₃₄ is generated during the oxidation of Mg–Al alloys, and at the same time, the oxidation layer of Mg–Al alloys breaks down during the oxidation process.²² This makes it possible to generate finer particles of MgAl₂O₄ from Mg–Al alloy. In this study, MgAl₂O₄ was synthesized using Mg–Al alloy as raw material, and its microstructure and spectral properties were characterized, the reaction mechanism was studied, and the possibility of using Mg–Al alloy to generate fine-grained MgAl₂O₄ was investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. In this paper, a Mg–Al alloy with a Mg/Al mass ratio of 50:50 was used as the raw material. It was supplied by Tangshan Weihao Magnesium Powder Co., Ltd. (Hebei, China). The used chemical reagent was of analytically pure grade.

A single-particle scanning electron microscopy (SEM) image for the Mg–Al alloy is shown in Figure 1. The alloy particles show a regular spherical morphology. It is obvious that trace amounts of nanosized particles appeared to cover the alloy surface, which might be related to the oxidation of magnesium or aluminum before use. Its particle size distribution is given in Figure 2.

The X-ray diffraction (XRD) pattern of the sample is shown in Figure 3. Only the presence of the Al₁₂Mg₁₇ phase is observed, and no diffraction peaks of Al or Mg are observed. Therefore, Al₁₂Mg₁₇ phase was formed, which is consistent

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with that reported in ref 22, that is, when the mass ratio of Mg to Al is 1:1, a high-purity intermediate alloy can be synthesized.

2.2. Synthesis of MgAl$_2$O$_4$. Mg−Al alloy powders were heated by a high-temperature electric resistance furnace (KJT1200-F6010LK2-G) from 50 to 1100 °C in air at 1 atm. Cylindrical ceramic crucibles with a height of 5 cm and a diameter of 10 cm were used to carry the powders. The air flow rate in the furnace was kept at 100 mL/min, and the heating rate was set at 20 °C/min. Approximately 10 g of alloy powder was used in each experiment. When the sample was heated to 1100 °C, the furnace shut down, and the temperature in the furnace naturally decreased to room temperature. Then, the samples were acid-washed using 37 vol % HCl solution at 60 °C for 5 h under magnetic stirring to remove the unwanted phases. Finally, the obtained powders were washed using distilled water and dried in an electric oven at 80 °C.

2.3. Characterization. The crystalline phase of the as-synthesized products and the raw material were examined by a X-ray diffractometer [Rigaku, SmartLab (3KW), Japan] with Cu target and Ka radiation. The morphological characteristics of MgAl$_2$O$_4$ powders were characterized by SEM (Hitachi, Regulus8100, Japan) and transmission electron microscopy (FEI, FEI Tecnai G2 F20, America). Energy-dispersive X-ray spectroscopy (EDAX Octane Elect, America) was used to observe the elemental distribution of the samples.
Transform infrared spectra (FT-IR) of the samples were recorded on a Nicolet iS50 FT-IR spectrometer (Thermo, America) in the scan range of 4000 to 400 cm⁻¹. UV–vis diffused reflectance spectra (DRS) of samples were registered on a Lambda 650 spectrometer (PerkinElmer, America) in the UV–vis region of 200–800 nm. The photoluminescence (PL) measurements were performed on an iHR320 spectrometer (Edinburgh Instruments, England) at room temperature. The particle size was obtained from Mastersizer 2000 (Malvern, England).

Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis (Mettler Toledo, Columbus, OH) were used to determine the reactions of the alloy powder in air or oxygen. Approximately 2.0 mg of the sample was heated at a rate of 20 °C/min from 50 to 1100 °C in a ceramic crucible. The flow rate of the air or oxygen was kept at 50 mL/min.

3. RESULTS AND DISCUSSION

3.1. Structural and Surface Analysis. Figure 4 shows the XRD pattern of the dried powder product. The XRD pattern with reference code (PDF#21-1152) of MgAl₂O₄ spinel is also shown in Figure 4. It can be seen that the sample presents a high-purity MgAl₂O₄ phase without any other impurities (Al₂O₃ and MgO). Basically, all the diffraction peaks of MgAl₂O₄ can be seen. The crystallite size of spinel phase is obtained using the parameters of the most intense (311) peak by the Scherrer formula:

\[ d = \frac{k\lambda}{(\beta \cos \theta)} \]  

where \( d \) is the crystallite size (nm); \( k \) is the correction factor, which is 0.943 here, considering the shape of the particles; \( \lambda = 1.54 \, \text{Å} \), \( \beta \) is full width of the diffraction peak; and \( \theta \) represents the Bragg angle. The crystallite size is calculated to be 37.78 nm.

The micromorphology of the synthesized magnesium aluminate spinel is illustrated in Figure 5. The microstructure of these MgAl₂O₄ particles shows that they are mainly composed of irregularly shaped particles. In addition, highly agglomerated particles are observed. Figure 6 shows the elemental distribution of the products. Al, Mg, and O are distributed uniformly in most of the particles. The energy-dispersive X-ray spectroscopy (EDX) image shown in Figure 7 indicates that the product is mainly composed of Mg, Al, and O elements and contains essentially no other impurities. The Au amount is negligible. In order to obtain more information on the morphology of the synthesized MgAl₂O₄, a transmission electron microscopy (TEM) survey was performed. The TEM images of the synthesized products are given in Figure 8. The size of synthesized MgAl₂O₄ is about 50 nm.

The particle size distribution of the synthesized MgAl₂O₄ spinel is given in Figure 9. \( D_v(50) \) of synthesized MgAl₂O₄ is 17.0 \( \mu \text{m} \), which seems to be different from the previously...
calculated value (37.78 nm) as well as the value observed in the TEM images (approximately 50 nm). This is mainly due to the agglomeration of product particles.

### 3.2. Spectral Analysis

The FT-IR spectrum is shown in Figure 10. In the IR spectra, the absorption bands at 532.28 and 698.09 cm\(^{-1}\) correspond to the stretching vibrations of Al–O and Mg–O–Al, respectively, which display the formation of MgAl\(_2\)O\(_4\) spinel. The two vibrational bands at 3423.48 and 1630.95 cm\(^{-1}\) may be attributed to the stretching and bending vibrations of the O–H bonds of surface-absorbed water molecules.\(^{23}\)

The UV–vis DRS of the product is shown in Figure 11a. As shown in Figure 11, the MgAl\(_2\)O\(_4\) sample exhibits UV absorption. The sample presents a weak absorption band at 252 nm. The band gap of MgAl\(_2\)O\(_4\) was estimated using the following equation:

\[
\alpha h\nu = A(h\nu - E_g)^n/2
\]

where \(\alpha\), \(h\), \(\nu\), \(A\), and \(E_g\) are the absorption coefficient, Planck's constant, light frequency, energy-independent constant, and band gap, respectively, and \(n\) is a constant which is 1 here.

Thus, as shown in Figure 11b, the band gap of MgAl\(_2\)O\(_4\) was deduced to be 4.02 eV.

### 3.3. Thermal Analysis

Figure 13 shows the TG-DSC curves of the Mg–Al alloy powders in air or oxygen. It can be seen that the oxidation of the alloy is a staged process whether conducted in air or oxygen. When the temperature increases above 400 °C, a small endothermic peak is first observed on the DSC curve, and the peak temperatures in O\(_2\) and air are 460.5 and 463.2 °C, respectively, which is caused by the eutectic melting of the alloy. Then, the DSC curve of the alloy can be divided into two stages. The first stage occurs after eutectic melting. An exothermic peak is observed in the DSC curve, and the sample mass increases. After the first stage, the DSC curve of the alloy experiences a short smoothing period. Then, the TG curve shows that the sample mass continues to increase. When the temperature reaches a certain value, a clear and sharp exothermic peak is again observed in the DSC curve. Due to the different gas environments, the oxidation process of alloy powder in oxygen or air is slightly different, which mainly manifests in the difference between the initial reaction temperature and the weight gain of the sample at each stage. Table 1 lists the parameters of the alloy oxidation process obtained from the TG-DSC curves.

### 3.4. Synthesis Mechanism of MgAl\(_2\)O\(_4\)

According to the TG-DSC curves of the sample in oxygen and air, the high-temperature oxidation process of the alloy is basically the same, which can be divided into two stages. To clarify the reaction process of the alloy at these two stages, the powders were heated to 500, 600, 700, 800, and 1000 °C in air by a high-temperature electric resistance furnace and then cooled to room temperature. The air flow rate in the furnace was kept at 100 mL/min, and the heating rate was set at 20 °C/min. Then, XRD was used to analyze the products. The results are shown in Figure 14. In the first stage of the reaction (~800 °C), as shown in Figure 14, when the Mg–Al alloy is heated to 500, 600, and 700 °C, the product is mainly composed of MgO and Al, which indicates that at this temperature, the alloy decomposes to produce Al and Mg. However, MgO forms more easily than Al\(_2\)O\(_3\) because Mg is more reactive than Al. The produced Mg...
is then oxidized by the oxygen in the air. Therefore, the oxidation process of the Mg−Al alloy at this stage can be written as:

$$\text{Al}_{12}\text{Mg}_{17} \rightarrow 12\text{Al} + 17\text{Mg}$$  \hspace{1cm} (3)

$$2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$$  \hspace{1cm} (4)

For MgO, the Pilling−Bedworth ratio is 0.73, which means that the oxide layer is loose and porous.24 Due to the porous form of MgO, oxygen can easily diffuse inward.

It seems that only the oxidation of magnesium occurs. However, this is not the case. According to previous studies,22 aluminum also undergoes partial oxidation at this stage. A portion of the Al will be oxidized to produce $\gamma$-$\text{Al}_2\text{O}_3$ between 600 and 800 °C, undetectable by XRD. The reaction process can be written as

$$4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$$  \hspace{1cm} (5)

As the temperature rises to 800 °C, the reaction enters the second stage, accompanied by formation of the MgAl$_2$O$_4$ spinel. The possible reaction for the formation of MgAl$_2$O$_4$ is

$$\text{Al}_2\text{O}_3(s) + \text{MgO}(s) \rightarrow \text{MgAl}_2\text{O}_4(s)$$  \hspace{1cm} (6)

The formation of MgAl$_2$O$_4$ powder from MgO and Al$_2$O$_3$ is a typical solid-state phase reaction.24 The thermodynamic conditions are the first element of this solid-state phase reaction. At room temperature, the reaction speed of MgO and

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**Table 1. Parameters of the Alloy Oxidation Process Read from the TG-DSC Curve**

| Atmosphere | Melting point °C | Onset temperature of the first stage °C | Mass change of the first stage % | Onset temperature of the second stage °C | Mass change of the second stage % |
|------------|------------------|----------------------------------------|---------------------------------|----------------------------------------|----------------------------------|
| O$_2$      | 460.5            | 479.2                                  | 31.1%                           | 647.8                                  | 67.4%                            |
| air        | 463.2            | 516.9                                  | 26.9%                           | 821.8                                  | 74.1%                            |

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**Figure 11.** (a) UV−vis DRS of the MgAl$_2$O$_4$ sample. (b) Plots of $(a\nu)^2$ versus energy $(\hbar\nu)$ for the band gap of MgAl$_2$O$_4$.

**Figure 12.** Photoluminescence spectra of the MgAl$_2$O$_4$ sample (excitation wavelength: 252 nm).

**Figure 13.** TG-DSC curves of Mg−Al alloy in O$_2$ (a) and air (b) at a heating rate of 20 K/min.
Al₂O₃ is extremely slow, and a rapid reaction can occur only when the temperature exceeds 1200 °C. With regard to the traditional method for synthesizing MgAl₂O₄ with MgO and Al₂O₃ powders, the particle sizes of the MgO and Al₂O₃ particles are generally micro-sized, and the synthesis progress usually takes hours or even days at approximately 1600 °C.

The synthesis mechanism of MgAl₂O₄ powder by the oxidation of a Mg−Al alloy is still the reaction between MgO and Al₂O₃. However, unlike the direct mixed powders of MgO and Al₂O₃, the oxidation of a Mg−Al alloy also includes the precipitation process of Mg and Al. At the early stage of the synthesis, a coating layer mainly composed of MgO and Al forms on the surface of the alloy particles. Because the temperature is relatively low at this time, it is certain that the layer exists in a solid state. For the high-temperature oxidation process of most metals, the coating layer formed on the particle surface will always hinder further oxidation. Shell−core models are often used to explain such a reaction process, as shown in Figure 15.

For the Mg−Al alloy, the oxidation layer formed at the first stage will also prevent further oxidation of the alloy. The Al₁₂Mg₁₇ core continues to decompose at high temperatures to produce liquid Mg and Al. Because Mg has a strong tendency to evaporate, the Mg vapor generated by Mg vaporization increases the pressure in the film. When the pressure of vapor becomes higher than the shell strength, the film ruptures, and external oxygen then reacts with the Mg and Al in the shell, once again forming a oxidation layer on the core surface. Thus, the reaction layer continues to grow until the Mg−Al alloy is completely converted into MgO and MgAl₂O₄. This is why the particle size of MgAl₂O₄ spinel synthesized by Mg−Al alloy is much lower than that of Mg−Al alloy itself.

4. CONCLUSIONS

In this research, MgAl₂O₄ powder was prepared by the SHS method using a Mg−Al alloy as the raw material. A series of characterizations of the synthesized MgAl₂O₄ were carried out. The XRD results show that the products are of high purity and well crystallized. The distribution of elements on the surface of MgAl₂O₄ is uniform, the particle shape is irregular, and the particle size is about 50 nm under TEM. The spectral

Figure 14. XRD patterns of synthesized powders at different termination temperatures.

Figure 15. Synthesis mechanism of MgAl₂O₄ by Mg−Al alloy.
properties of the prepared MgAl₂O₄ were studied using FT-IR, UV–vis DRS, and PL spectrometry. The synthesis mechanism of MgAl₂O₄ powder by the Mg–Al alloy was discussed. The results show that the synthesis process can be divided into two stages. Oxidation of Mg and Al occurs in both stages. The second stage is mainly the formation of spinel phase. The continuous rupture and growth of the reaction layer during the reaction may be the reason why the size of product MgAl₂O₄ particles is much lower than that of Mg–Al alloy.

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Notes
The authors declare no competing financial interest.

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