Study on Sinterability of Magnesium Aluminate Spinel Powders Prepared by Different Technologies

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Abstract. In this paper, the phase, structure and sinterability of magnesium aluminate spinel powders prepared by the chemical co-precipitation, low temperature combustion and solid phase reaction methods were studied. The results show that the uniform nanometer magnesium aluminate spinel powders are prepared from precursor via the chemical co-precipitation, calcined at 700°C. Using the low temperature combustion method, the agglomeration, complete crystalline nanometer magnesium aluminate spinel powders are prepared at the thermal explosion temperature of 400°C. For the magnesium aluminate spinel micrometre powders synthesized by the solid phase reaction method, the phases are mainly spinel with a little of periclase and corundum phase. The sinterability of powders prepared by chemical co-precipitation method is the best, but that of powders synthesized by low temperature combustion and solid phase reaction methods are poor.

1. Introduction
Magnesium aluminate spinel (MgAl₂O₄) exhibits many excellent properties, such as high melting point, good mechanical strength both at room and evaluated temperatures, high resistance to chemical attack, good thermal shock resistance, high catalytic properties, excellent optical and dielectric properties. It has been widely used in many industrial areas, e.g. refractory materials [1], catalyst supports [2], transparent ceramics [3]. Due to the good chemical stability and high melting point, MgAl₂O₄ materials are difficult to be sintered. The particle size and agglomeration of powders directly affect the sinterability of MgAl₂O₄. Therefore, synthesis of fined MgAl₂O₄ powders is important for fabricating MgAl₂O₄ bulk. Several important techniques that have been extensively used for preparing MgAl₂O₄ powders include solid-state synthesis, co-precipitation, sol-gel process, molten salt synthesis and combustion synthesis. Each of the above techniques has own advantages and disadvantages [4-11].

In this study, MgAl₂O₄ powders were prepared by co-precipitation technique, low temperature combustion synthesis (LCS) and solid-state reaction method. Their properties, such as phase composition, microstructure and so on, were compared with each other. The sinterability of MgAl₂O₄ powders prepared by different techniques were examined through testing the density of bulk with different powders.

2. Experimental
MgAl₂O₄ powders were prepared by co-precipitation method using AR grade MgCl₂·6H₂O, AlCl₃·6H₂O and (NH₄)₂CO₃ as the starting materials. Stoichiometric amounts of MgCl₂·6H₂O and AlCl₃·6H₂O were mixed and dissolved in deionized water. (NH₄)₂CO₃ solution was added dropwise to the mixed solution under constant magnetic stirring, and adjusting pH value around 11 with ammonia.
solution. After precipitation, the slurry was stirred for another 30 min. Subsequently, the precipitate was filtered and was dried at 100°C for 24h. Then the dried precipitate was calcined at 700°C, 800°C and 900°C for 2h, respectively.

MgAl_2O_4 powders were prepared by LCS process using AR grade Mg(NO_3)_2·6H_2O, Al(NO_3)_3·9H_2O and CO(NH_2)_2 as the starting materials. The molar ratio of Mg(NO_3)_2·6H_2O : Al(NO_3)_3·9H_2O : CO(NH_2)_2 was 1:2:6.67 based on propellant chemistry theory. All the reactants were mixed sufficiently in an agate mortar, and grinded to form homogeneous paste-like substance. Then the paste was ignited at 400°C, 500°C and 600 °C in a muffle furnace. As soon as the reaction was over, the powders were taken out of the furnace and cooled in air.

MgAl_2O_4 powders were derived from commercial Al_2O_3 and laboratory-made light calcined MgO through solid-state synthesis. Stoichiometric amounts of MgO and Al_2O_3 were ground in the ball mill for 24h. Next, the mixed starting materials were calcined at 1000 °C, 1100°C and 1200 °C for 2 h, respectively.

The powders prepared as mentioned above were pressed into pellets of 20 mm in diameter and 5 mm in height at 200 MPa. The pellets were dried at 110°C for 12 h, then sintered at 1600 °C for 3 h. The sintered specimens were cooled inside the furnace under air atmosphere.

The phases of MgAl_2O_4 powders were analyzed by X-ray powder diffraction (XRD, Cu target, 30 kV and 30 mA). The morphology of powders and fracture surface of sintered specimens were observed by scanning electron microscopy (SEM). Moreover, the density of sintered specimens was measured.

![XRD patterns of MgAl_2O_4 powders prepared by co-precipitation.](image)

**Figure 1.** XRD patterns of MgAl_2O_4 powders prepared by co-precipitation.

3. Results and Discussion

3.1. Phase of MgAl_2O_4 powders

The XRD patterns of MgAl_2O_4 powders prepared by co-precipitation method are shown in Figure 1. It is observed that the powders calcined at the temperature between 700°C and 900°C was single-phase MgAl_2O_4 spinel, and the intensity of the peak increased with increasing of the calcination temperature.

The XRD patterns of MgAl_2O_4 powders prepared by LCS are shown in Figure 2. As shown in Figure 2, the pure MgAl_2O_4 phase already appears with the weak and broadened characteristic diffraction peaks as the ignition temperature was 400°C, and the characteristic peaks become narrower...
and stronger with increasing ignition temperature. Increasing ignition temperature means that heating rate of reactants is rapid, and evaporation rate of the water in reactants is quick, so the flame temperature is high, and then is helpful to synthesis of MgAl₂O₄ spinel.

![XRD patterns of MgAl₂O₄ powders prepared by LCS.](image1)

**Figure 2.** XRD patterns of MgAl₂O₄ powders prepared by LCS.

![XRD patterns of MgAl₂O₄ powders prepared by solid-state reaction.](image2)

**Figure 3.** XRD patterns of MgAl₂O₄ powders prepared by solid-state reaction.

The XRD patterns of MgAl₂O₄ powders prepared by solid-state reaction are shown in Figure 3. As the calcination temperature is 1000 °C, we can see that the MgAl₂O₄ phase has begun to appear, but there are still lots of unreacted Al₂O₃ and MgO, which indicates that the reaction between MgO and Al₂O₃ is not complete enough; Even at temperature of 1100 °C, there are still much MgO residue; When the temperature is raised to 1200 °C, MgAl₂O₄ is formed in a large amount, and only a small amount of Al₂O₃ and MgO are residual. Béclin’s research [12] showed that the calcination temperature...
was controlled at about 1100-1200 °C, the activity of MgAl₂O₄ powders was higher. If the calcination temperature was further increased, the activity would be decreased instead of increasing. Therefore, the highest calcination temperature investigated in this study is 1200 °C.

3.2. Morphology of MgAl₂O₄ powders

The SEM photomicrographs of the powders prepared by co-precipitation are shown in Figure 4. It can be seen that all of powders have near spherical shape and roughly similar particle size (nanoscale), and the powders are loosely agglomerated and fairly uniform. In this study, the phases of the MgAl₂O₄ precursor analyzed by XRD are mixture of Mg₆Al₃(OH)₁₄·3H₂O and Mg₅(CO₃)₄(OH)₄·24H₂O. During the powders calcined, the decomposition of carbonaceous material produces gases, then the gases generally prevents from agglomeration of powders during the reaction.

![Figure 4](image-url)

**Figure 4.** SEM images of MgAl₂O₄ prepared by co-precipitation calcined at 700 °C(a), 900 °C(b).

The SEM photomicrographs of the powders prepared by LCS are presented in Figure 5. At the ignition temperatures are 400°C and 600°C. The size and morphology of powders are greatly affected by the ignition temperature. When the ignition temperature is 400°C, the particle size of powders is less than 50nm, and the morphology is spherical. While some big plate-like or rod shape particles are observed, the size of them are over 500 nm, as the ignition temperature is 600°C.

![Figure 5](image-url)

**Figure 5.** SEM images of MgAl₂O₄ prepared by LCS ignited at 400°C (a), 600°C (b).

The SEM photomicrographs of MgAl₂O₄ powders prepared by solid-state reaction at different temperatures are shown in Figure 6. It can be seen that the particle size of MgAl₂O₄ powders is about 1μm, and relatively uniform, as the calcination temperature is 1000°C. While the calcination temperature is increased to 1200°C, the micro-morphology of powders is irregularity and the particle size is non-uniform, the particle size of some powders is about 10μm.
Figure 6. SEM images of MgAl$_2$O$_4$ prepared by solid-state reaction calcined at 1000 °C (a), 1200 °C (b).

Figure 7. Density of sintered pellets derived from different MgAl$_2$O$_4$ powders.

Figure 8. Fracture microstructure of pellets sintered at 1600°C, (a) co-precipitation, (b) LCS, (c) solid-state reaction

3.3. Sinterability MgAl$_2$O$_4$ powders
The bulk density and fracture microstructure of sintered pellets are shown in Figure 7 and Figure 8, respectively.

From Figure 7, it can be seen that the density of specimens is affected strongly by synthesis methods. The bulk density of specimens prepared by co-precipitation is the highest, the apparent porosity is the correspondingly lowest. While the density of specimens prepared by LCS is the lowest. Figure 8 also shows the same tendency. It’s well known that the particle size, uniformity and agglomeration degree of ceramic powders directly affect the sintering properties of the materials. The powders with small particle size, no obvious agglomeration, and narrow particle size distribution have
good sinterability. Otherwise, coarse particle size, strong agglomeration and poor particle size uniformity, the sintering properties is poor. Through the SEM photomicrographs of the powders prepared by three different methods, the particle size of MgAl$_2$O$_4$ powders prepared by co-precipitation is fine and relatively uniform. The average particle size of powders prepared by LCS is relatively smaller than that of powers prepared by solid-state reaction, but it’s particle uniformity is poorer, and the agglomeration is relatively stronger, which leads to the formation of large pores in the sintering process, and thus the sintering properties is relatively poor.

4. Conclusions
(1) The MgAl$_2$O$_4$ powders prepared by co-precipitation with fine particle size and narrow particle size distribution shows the best properties, possesses the high density of bulk specimens.
(2) The complete crystalline nanometer MgAl$_2$O$_4$ powders can be prepared by LCS at the ignition temperature of 400 °C, while the sinterability of the powders is poor.
(3) The phases of powders prepared by solid-state reaction at calcined temperature 1200 °C are mainly spinel with a little of periclase and corundum phase. Due to the coarse particle and poor particle size uniformity, the sinterability of the powders is not good.

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