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Combustion Synthesis of $MgSiN_2$ Powder at Different Nitrogen Pressures

Mingu Zhou[1], Senjing Zhang[2], Qingda Li[2], Xuemei Yi[2*]

[1]Institute of Water-Saving Agriculture in Arid Areas of China (IWSA), Yangling, China
[2]College of Mechanical and Electronic Engineering, Northwest A&F University, Yangling, China
Email: *xuemei_yi@nwsuaf.edu.cn

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Abstract

$MgSiN_2$ powders have been synthesized by combustion synthesis (CS) using Mg and Si_3N_4 as starting materials at different nitrogen pressures. The CSed powders were then sintered by spark plasma sintering (SPS) to obtain dense bulk $MgSiN_2$ product. Analysis of the CSed powder using X-ray diffraction (XRD) revealed single-phase $MgSiN_2$ was obtained by CS method. However, the CSed product can be divided into three distinct parts according to its color. Scanning electron microscopy (SEM) observation revealed the grain size and crystallinity decrease gradually from the center to the outer layer. Some small grains clustered together to form larger particles, and there were a large number of pores among the clusters. The grain size seemed increasing with the increase of nitrogen pressure. The bulk density of CS-SPSed $MgSiN_2$ was 3.11 g/cm^3, Vickers hardness was 1673.1 kgf/mm^2, and thermal diffusivity was 8.718E^{-2} cm^2/s.

Keywords

Magnesium Silicon Nitride, Combustion Synthesis, Microstructure, Thermal Diffusivity

1. Introduction

In recent years, magnesium silicon nitride ($MgSiN_2$) has been attracted great interest due to the crystal structure is similar to aluminium nitride (AlN). Compared with AlN, $MgSiN_2$ is a simple covalent insulator, and shows more excellent mechanical properties than AlN ceramics [1] [2] [3]. $MgSiN_2$ has many attractive properties such as high thermal conductivity, low dielectric constant, high hardness, high thermal stability, good oxidation resistance (up to 920˚C) and high electrical resistance at room temperature [4] [5]. All of the above features

make $MgSiN_2$ very suitable for the electronic substrate/package and heat radiator. $MgSiN_2$ has been successfully used as effective sintering additive of nitrogen ceramics or growth promoter of β-Si_3N_4 rod crystal [6] [7] [8] [9]. $MgSiN_2$ is also considered to be a promising luminescent material for light emitting diode (LED) applications [10] [11].

$MgSiN_2$ can be prepared by various methods, such as carbothermal reduction [12], direct nitridation [13] [14] [15], hot-pressing [16], solvothermal method by the reaction of $SiCl_4$, N_2H_4·HCl and Mg [17], the solid-state metathesis route using SiO_2 and Mg_3N_2 as reactants [18]. However, most of these methods usually require high-energy consumption, high-temperature, long-time treatment.

Combustion synthesis (CS), also called self-propagating high-temperature synthesis (SHS) is well-know to prepare a series of advanced materials, due to its energy-efficient, time-saving, low processing cost, mass production, high production rate [19] [20]. Thus, preparation of $MgSiN_2$ by combustion synthesis in nitrogen gas was also widely studied using different starting materials (Mg/Si_3N_4, Mg/Si, Mg_2Si) as reactant [21]. However, the reaction mechanism is still unclear during combustion synthesis process for preparation of $MgSiN_2$.

Sintering methods such as hot press sintering and reaction sintering have been previously used to produce $MgSiN_2$ ceramic. As a promising rapid and effective densification technique, spark plasma sintering (SPS) have been previously used to produce some ceramics as well as other hard materials. However, to the author's knowledge, so far, there is no information on the use of this technique to synthesize $MgSiN_2$.

In this paper, $MgSiN_2$ powder was prepared by combustion synthesis between Mg and Si_3N_4 without additive, using a combustion synthesis apparatus in different N_2 pressures. Then the CSed powders were sintered using spark plasma sintering (SPS) system for obtaining bulk $MgSiN_2$ product. We hope this research can pave the way for prepare high thermal conductivity of $MgSiN_2$.

2. Experimental Procedure

2.1. Synthesis of $MgSiN_2$ Powder

Mg (purity, 180 μm in size) and α-Si_3N_4 (purity, 0.5 μm in size) powders were used as raw materials. The chemical reaction for the synthesis of $MgSiN_2$ from the above mentioned starting materials can be shown as follows:

$$3Mg + Si_3N_4 + N_2 \rightarrow 3MgSiN_2 + \Delta H \quad (1)$$

when the raw mixtures are ignited, the heat released (ΔH) will keep the reaction going to the end. The schemata for the step-wise synthesis were shown in **Figure 1**. $MgSiN_2$ powders were prepared by the raw materials of Mg and Si_3N_4 with the mole ratio of 3:1. Then, the reactant mixtures with the compositions shown in **Table 1** were mechanically milled by a planetary ball mill for 15 min in an alumina container of 250 ml. Silicon nitride balls were ∅ 5 mm in diameter as medium, and the weight ratio of ball to powder was 10:1. The ball milling was processed at 200 rpm. After milling, the mixture was charged into a cylindrical

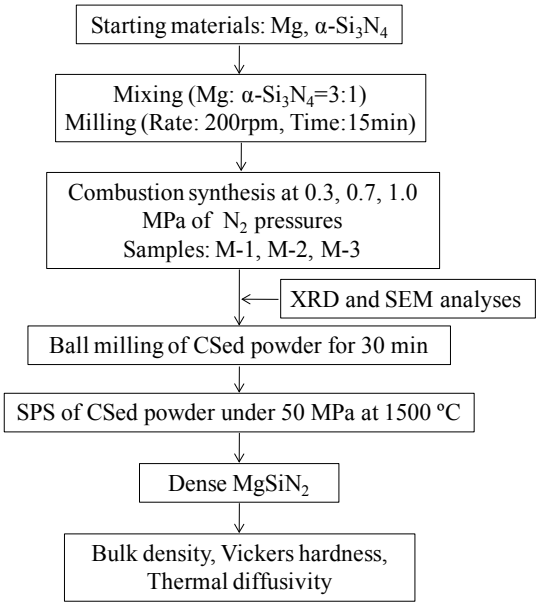

Figure 1. Flow chart of the experimental procedure for synthesizing $MgSiN_2$.

Table 1. Compositions of the raw reactants and experimental conditions.

Sample	Composition (mole ratio)	P_{N2} (MPa)
M-1	$Mg:Si_3N_4$ = 3:1	0.3
M-2	$Mg:Si_3N_4$ = 3:1	0.7
M-3	$Mg:Si_3N_4$ = 3:1	1.0

graphite crucible (diameter: 40 mm; length: 65 mm). And after the procedure of evacuation, nitrogen gas (99.99% in purity) was finally introduced to raise the pressure to preset condition into the chamber. The combustion reaction was triggered by igniting the sample by passing an electric current through a carbon foil placed on the top of sample. One W-Re thermocouple was inserted into the center of the sample to record the combustion temperature profile. The apparatus can be found other else [22].

2.2. Sintering

The CSed powder was ball milled for 30 min for SPS using the planetary ball milling. After milling, the powders were compacted into a carbon die of 10 mm in inner diameter and sintered by a SPS system under 50 MPa of compressive stress. The resulting compacts heated from room temperature to 600˚C in 5 min, and then were heated to 1500˚C at a rate of 30˚C/min, and maintained at this temperature for 10 min before turning off the power.

2.3. Characterization

The phases of the combustion products were identified by an X-ray diffraction (XRD) analyzer (Mini Flex, Rigaku Corporation, Tokyo, Japan). The morphologies of the reaction products were investigated by scanning electron microscopy

(SEM) (FE-SEM JSM-7400F, JEOL, Tokyo, Japan). The bulk density of the SPSed specimens was measured according to the Archimedean principle, using distilled water as the medium. The Vickers hardness was measured using a Vickers microhardness tester with a diamond indenter of regular pyramid with an opposite angle of 136˚. The thermal diffusivity was measured by the laser-flash method (TC-7000, ULVAC Sinku RikoCo., Yokohama, Japan) at room temperature.

3. Results and Discussion

Figure 2 shows the temperature history of sample M-2 at CS under 0.7 MPa N_2 pressure, and the thermal couples were set at the center of the sample. It can be seen, only in several seconds, the temperature sharply reached its apex of 1840˚C, and then began to decrease. It nearly held about 100 s above 1091˚C, which is the boiling point of Mg.

The product picture of sample M-2 at CS under 0.7 MPa N_2 pressure is shown in Figure 3. All of the products for M-1, M-2, and M-3 showed similar. The cross section of the product can be clearly divided into three parts according to the color. The outside was dark and the center part was grey-brown, while the intermediate layer was white.

The XRD patterns of the central parts for samples M-1, M-2, and M-3 are shown in Figure 4. It can be seen that all of the central parts for the three samples are pure $MgSiN_2$ as the N_2 pressure increasing from 0.3 MPa to 1.0 MPa. The XRD patterns of different parts for sample M-2 are shown in Figure 5. For

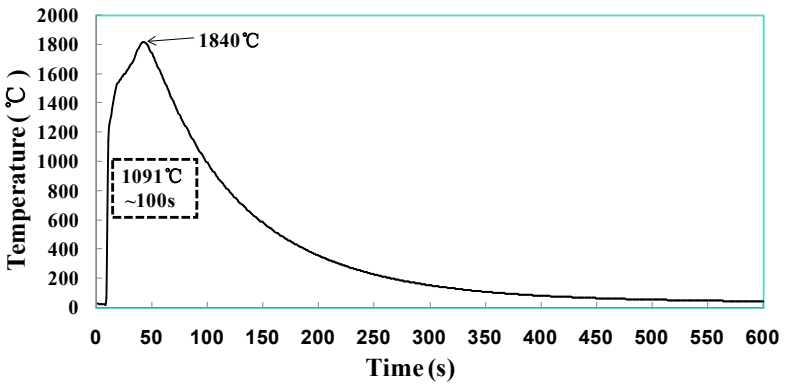

Figure 2. Temperature history of sample M-2 at CS under 0.7 MPa N_2 pressure, the thermal couples were set at the center of the sample.

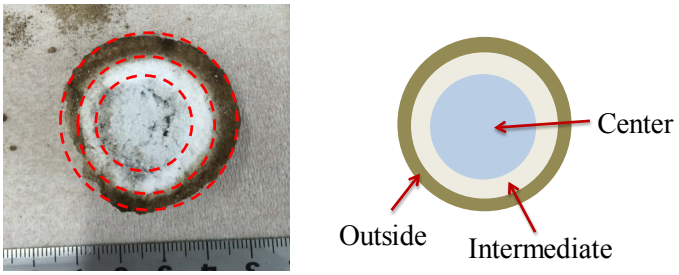

Figure 3. The portrait of sample M-2 for CS at 0.7 MPa N_2 pressure.

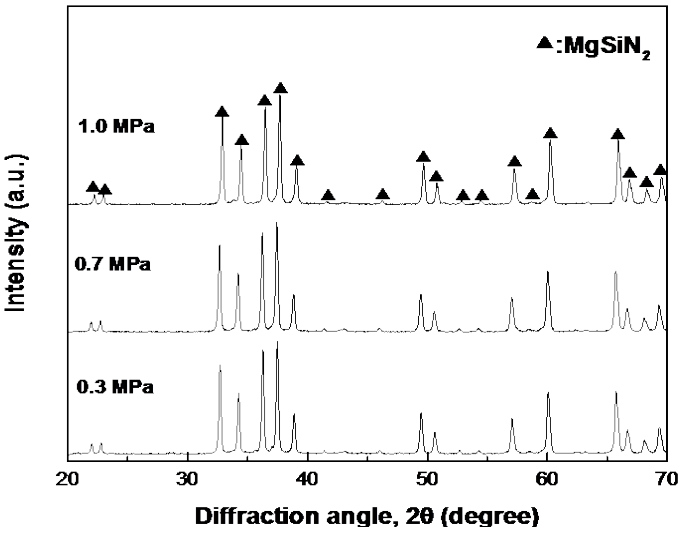

Figure 4. XRD patterns of combustion product synthesized at different N_2 pressures.

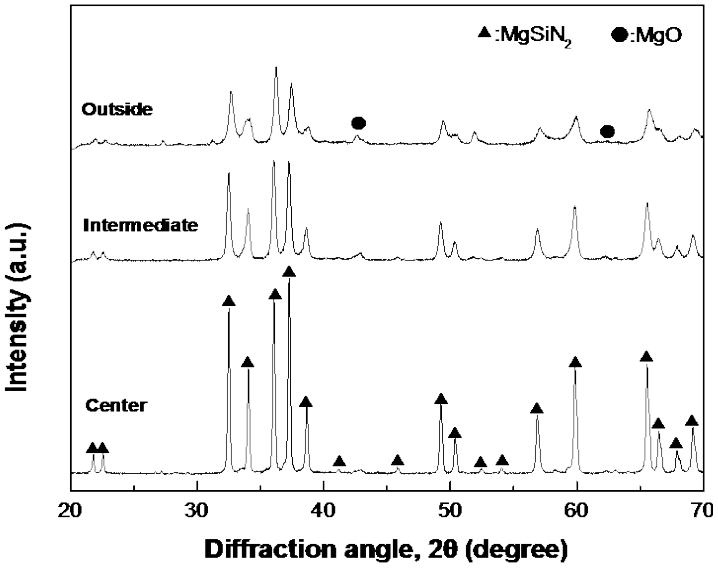

Figure 5. XRD patterns of the combustion product of sample M-2.

all of the three parts, the major phase was $MgSiN_2$. The XRD peaks of the central part are very sharp, while those of the outer part are relatively flat, which indicates the degree of crystallization of $MgSiN_2$ gradually decreasing from inside to outside. A small amount of MgO peaks appeared in both intermediate and outside parts. Combined with the temperature history shown in **Figure 2**, due to the high temperature at central part, Mg evaporated over 1091˚C. The Mg vapor diffused from center to outside of the sample. In addition, a heavy odor was smelled when the CS equipment was opened. Combining the above phenomena, when the combustion synthesis reaction is ignited, the target product $MgSiN_2$ is obtained according to above mentioned Equation (1). However, a small amount of Mg vapor diffuses into the outer layer and reacts with nitrogen to obtain Mg_3N_2 due to the high temperature in the core of the sample. When the furnace

is opened, Mg_3N_2 reacts with water in the air to obtain MgO and ammonia. The reaction can be expressed as follows:

$$3Mg + N_2 \rightarrow Mg_3N_2 \quad (2)$$

$$Mg_3N_2 + 6H_2O \rightarrow 3MgO + 2NH_3(g) \quad (3)$$

Furthermore, the oxygen may also come from the oxygen impurity of starting materials or nitrogen gas. Although the color of the outer layer was greenish yellow, no Mg_3N_2 phase peaks was detected by XRD, possibly due to too little content or too low crystallinity. Another possible reason for this phenomenon may be the decomposition of magnesium silicon nitride [23].

The SEM images of the products synthesized at different N_2 pressure are shown in Figure 6. All of the three samples showed that some small grains clustered together to form larger particles, and there were a large number of pores among the clusters. The average diameter of the small grains looked smaller than 1μm. However, it seemed that the grain size tends to increase with the increase of nitrogen pressure based on the SEM pictures. Figure 7 shows the SEM images of different parts for sample M-3. It can be seen that the grain size and crystallinity decrease gradually from the center to the outer layer due to temperature gradient between different parts.

Table 2 summarizes the characteristics of the CS-SPSed $MgSiN_2$ products. bulk density was 3.11 g/cm^3, Vickers hardness was 1673.1 kgf/mm^2, and thermal diffusivity was 8.718E^{-2} cm^2/s.

Table 2. Properties of the bulk $MgSiN_2$ sintered at 1500˚C by spark plasma sintering.

Phase composition From XRD	Bulk density (g/cm^3)	Thermal diffusivity (cm^2/s)	Vickers hardness (kgf/mm^2)
$MgSiN_2$	3.11	8.718E−2	1673.1

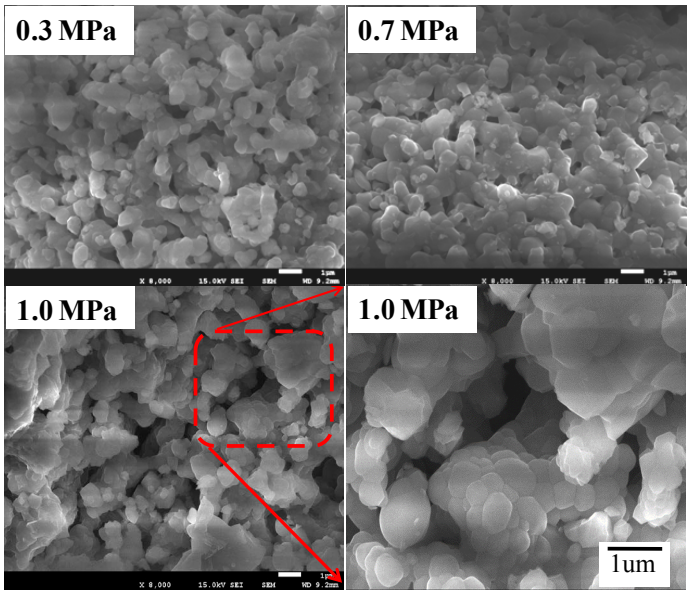

Figure 6. SEM images of combustion products synthesized at different N_2 pressures.

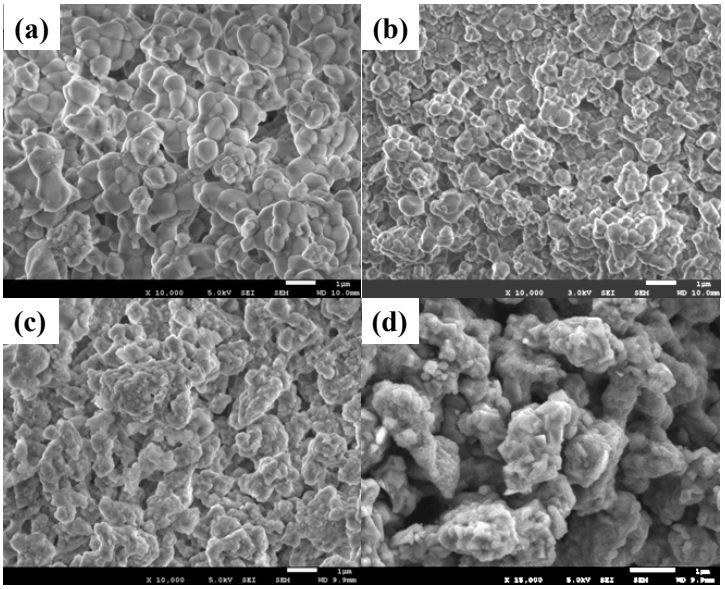

Figure 7. SEM images of sample M-3: (a) Center; (b) Intermediate; (c) Outside; (d) Magnification of (c).

4. Conclusion

Single-phase $MgSiN_2$ was synthesized by combustion synthesis method under N_2 pressures of 0.3 - 1.0 MPa using Mg/Si_3N_4 as reactants. The CSed product can be divided into three distinct layers according to its color. SEM observation showed the grain size decreased gradually from the center to the outer layer. Some small grains clustered together and formed larger particles, and there were a large number of pores among the clusters. The bulk density of CS-SPSed $MgSiN_2$ was 3.11 g/cm^3, Vickers hardness was 1673.1 kgf/mm^2, and thermal diffusivity was $8.718E^{-2}$ cm^2/s.

Funding

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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