

Synthesis of MgSiN₂ Powders from the Mg-Si System

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Abstract

Magnesium silicon nitride (MgSiN₂) was synthesized without any additives under a nitrogen gas flow (200 mL/min) using a nitriding method. The effects of temperature and holding time on its purity and morphology were investigated. A single-phase MgSiN₂ powder was obtained at 1350°C for 1 h and 1250°C for 11 h. However, the decomposition of MgSiN₂ occurred at 1450°C, suggesting that the optimum temperature for the preparation of MgSiN₂ from Mg-Si system was 1350°C. The phase purity, morphology, size of the product and elemental composition of the samples were detected by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy spectrometer (EDS), respectively. The evaporation of Mg and Si resulted in the formation of many voids in the blocky product. The temperature gradient promotes the growth of MgSiN₂ on the surface of massive products along the tip. The concentration gradient of Mg and Si vapors in the void resulted in the columnar growth of MgSiN₂.

Keywords

Nitride Materials, Crystal Growth, X-Ray Diffraction, Mg-Si System

1. Introduction

In recent years, ternary nitrides have been widely investigated due to their higher functionality than binary nitrides. β -SiAlON, Si₃N₄, and AlN all exhibit excellent thermal performances [1]-[7]. The crystal structure of MgSiN₂ belongs to the orthorhombic system similar to AlN; however, the mechanical properties of MgSiN₂ are superior to those of AlN. Thus, MgSiN₂ has attracted extensive attention owing to its high fracture toughness (3 MPa·m^{1/2}), high stress intensity (280 MPa), high hardness (20 GPa), high-temperature electrical insulation,

high-temperature oxidation resistance (up to 920°C), excellent thermal conductivity, etc. [8]-[13]. In view of its theoretical thermal conductivity value of up to 75 W/m·K, MgSiN₂ should replace the AlN material as a new generation of ceramic materials with high thermal conductivity [14]. It can also be used as substrate material, packaging material, fluorescent material, for sintering aid of non-oxide ceramics with high thermal conductivity, and as growth additive in the combustion synthesis of β-Si₃N₄ rod crystals. Therefore, it is considered a very promising engineering and functional ceramic material [15]-[25].

In the past few decades, the preparation of MgSiN₂ using different methods and raw materials has been widely studied. Uchida *et al.* [26] obtained single-phase MgSiN₂ by nitridation of Mg₂Si at 1400°C for 1 h. Bruls *et al.* [27] used Mg₃N₂/Si₃N₄ as starting mixture to obtain MgSiN₂ with oxygen content of only 0.1 ± 0.1 wt%. Mg and Si have also been used as raw materials to synthesize MgSiN₂ at 1250°C for 16 h; however, no single-phase products were obtained. Lences *et al.* [28] synthesized MgSiN₂ by direct nitridation of complex mixtures consisting of Mg/Si/Si₃N₄/Mg₂Si, and reported the thermal analysis, phase composition, and characterization of the resulting MgSiN₂ powders. Khajelakzay *et al.* [9] prepared MgSiN₂ nanopowders by mechanical alloying and heat treatment in two steps, using Mg/Si as starting mixtures and adding a small amount of stearic acid. Yang *et al.* [29] synthesized single-phase MgSiN₂ powders starting from Mg/Si₃N₄ by combustion synthesis, followed by acid washing. The preparation of MgSiN₂ by carbothermal reduction was also reported [30]. The synthesis of MgSiN₂ by a solvothermal method used SiCl₄, N₂H₄·HCl, and Mg as starting materials [10]. The use of SiO₂ and Mg₃N₂ as reactants was described to synthesize MgSiN₂ by a solid-state metathesis route [31]. However, no single-phase MgSiN₂ has yet been prepared by direct nitridation at low temperatures (1250°C), and studies on the effect of holding time on the purity and morphology of MgSiN₂ are lacking.

In this study, single-phase MgSiN₂ powders were successfully prepared by nitridation of the Mg-Si system, and the effects of temperature and holding time on the purity and morphology of the products were also investigated. The purpose of this study was to obtain the desired products at low temperature, as well as to shorten the required time of nitridation. We believe that this discovery can pave the way for preparing MgSiN₂ with low energy consumption.

2. Materials and Methods

Mg (>99 wt% purity, Aldrich Reagent Co. Ltd.) and Si (99.99 wt% purity, 300 mesh, Adamas Reagent Co. Ltd.) were used as starting materials to synthesize MgSiN₂. The raw Mg and Si materials were mixed and grinded in an agate mortar with a mole ratio of 2:1. Due to the evaporation of Mg, the Mg/Si value deviated from the stoichiometric ratio, a large amount of Mg was consumed. Subsequently, the mixed powders were placed in an alumina crucible, which was covered with a carbon cloth; the mixtures were also covered with a carbon cloth

to prevent Mg from evaporating. Then, the crucible containing the mixed powders was sealed and placed in the middle part of a high temperature resistance furnace. After vacuum was pumped, the furnace was filled with nitrogen at a flow rate of 200 mL·min⁻¹, and heated at temperatures between 500°C and 1450°C for different holding time. The heating rate was 5°C·min⁻¹ for all samples.

After thermal treatment, the products were ground using a mortar and pestle before testing. The phase composition of the samples was examined by using an X-ray powder diffraction (XRD) analyzer (D8 ADVANCE A25, Bruker Corporation, Germany) with Cu K α radiation, operating at 40 kV and 40 mA. The particle sizes and morphologies of the synthesized powders were determined using scanning electron microscopy (SEM) (Nova Nano SEM 450, FEI Corporation, America).

3. Results and Discussion

The XRD patterns of the products synthesized within the temperature range of 500°C - 1450°C starting from Mg and Si are shown in **Figure 1**. At 500°C, Mg and Si did not react efficiently and only a little amount of Mg₂Si was formed. As the temperature increased, Mg and Si reacted to generate a large amount of Mg₂Si at 750°C, although some unreacted Si remained. At 900°C MgSiN₂ formed; it is possible that Mg₂Si reacted with N₂ to afford MgSiN₂ and Mg₃N₂. The formation of Mg₂Si from Mg and Si probably occurred as follows:

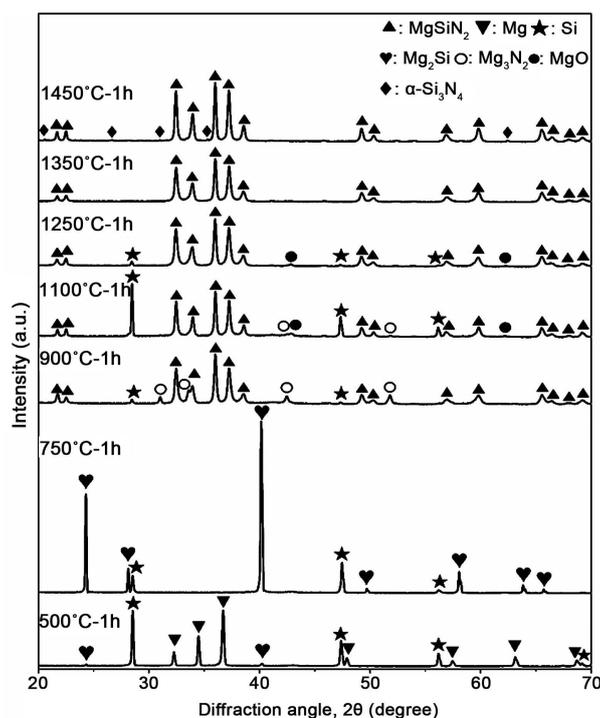
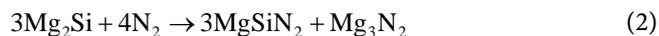
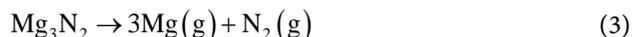


Figure 1. XRD patterns of the products synthesized at different temperatures.

The reaction between Mg_2Si and N_2 may take place as follows:



A large amount of Si was present at 1100°C ; given that the melting point of Mg_2Si is 1102°C , it can be speculated that the decomposition of Mg_2Si occurred at this temperature. As the temperature continued to rise, a single-phase MgSiN_2 appeared at 1350°C . The high temperature allowed the starting materials to react completely to generate the nitride, causing the evaporation of the MgO present in the reaction mixture as well as the decomposition of the Mg_3N_2 product into N_2 and Mg (g) as follows:



The formation of MgO may be due to the presence of oxygen impurities in the raw material, oxygen pickup during mixing, and oxygen in the N_2 atmosphere; thus, the oxygen reacts with Mg or Mg_3N_2 to form MgO . At 1450°C , MgSiN_2 decomposed to give rise to Si_3N_4 . When the experiments were conducted at 1450°C for 3 h, the content of Si_3N_4 increased. **Figure 2** shows the SEM images and EDS analysis results of the products synthesized at 1450°C after holding for (a) and (b) 1 h, (c) and (d) 3 h. The EDS results show that the hexagonal prism-like crystals of **Figure 2(a)** and **Figure 2(c)** are Si_3N_4 . Pt exists because the samples were plated with platinum before testing samples for EDS, the Mg exists because a small amount of MgSiN_2 is attached to the surface of the Si_3N_4 in the test area. Upon increasing of the holding time, the crystal size of MgSiN_2 became larger. Previous studies described that the thermal stability of MgSiN_2 is up to 1400°C [32]. Compared with combustion synthesis method, due to the combustion temperature greatly exceeds the melting point of Mg and maintained for

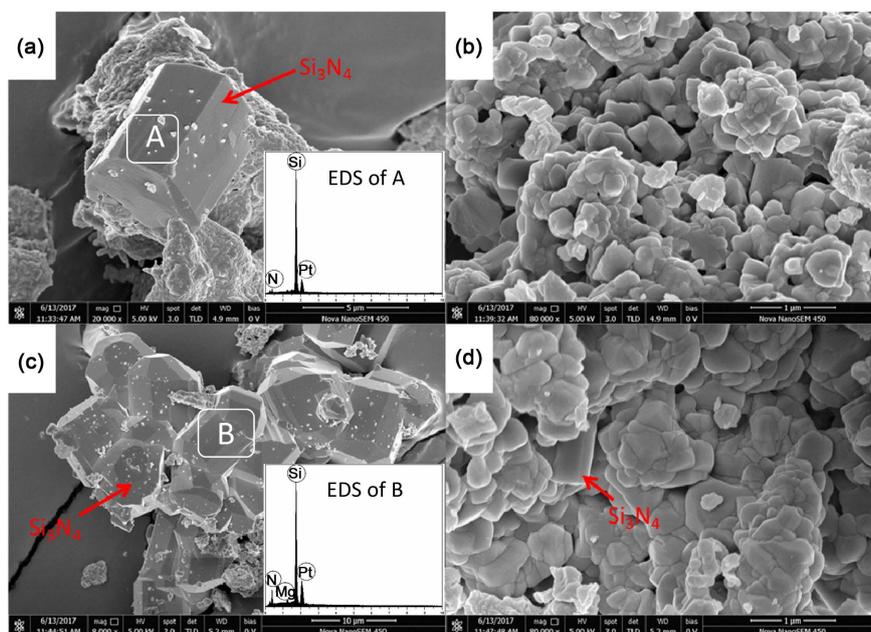
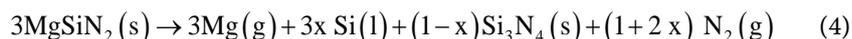


Figure 2. SEM images and EDS analysis results of the products synthesized at 1450°C after holding for (a) and (b) 1 h; (c) and (d) 3 h.

a long time, resulting in a large number of evaporation of magnesium, so the product in addition to MgSiN_2 also appeared in Si, MgO and not identified phases [11]. Oxygen impurities will reduce the thermal conductivity of the product, but the MgO can be washed off by acid washing [29]. As of now, there has been no literature to report that Mg and Si can be synthesized by combustion synthesis to obtain a single phase of the MgSiN_2 powder.

Figure 3 shows the XRD patterns of the products synthesized at 1350°C for different holding time. It was found that the powder of the middle part of the sample was measured and the result was single phase MgSiN_2 . Although after 8 h some black powders appeared around the product that were completely separated from it. **Figure 4** shows the XRD pattern of these black powders, which suggested the presence of some Si_3N_4 and Si impurities in addition to MgSiN_2 . This indicates that not only the decomposition of MgSiN_2 into Mg and Si_3N_4 occurred owing to the long reaction time, but also Si_3N_4 decomposed according to the following reaction [32]:



Furthermore, a small amount of white fibrous powder was observed around the crucible upon holding for a long time; although the amount was too small to be tested, it most likely consisted of MgO. The oxygen in the gas atmosphere reacted with Mg or Mg_3N_2 to form MgO.

We also attempted to obtain MgSiN_2 at low temperature (1250°C). Therefore, different amounts of urea were added to the raw materials to promote nitridation and reduce the impurities, but this did not lead to major improvements.

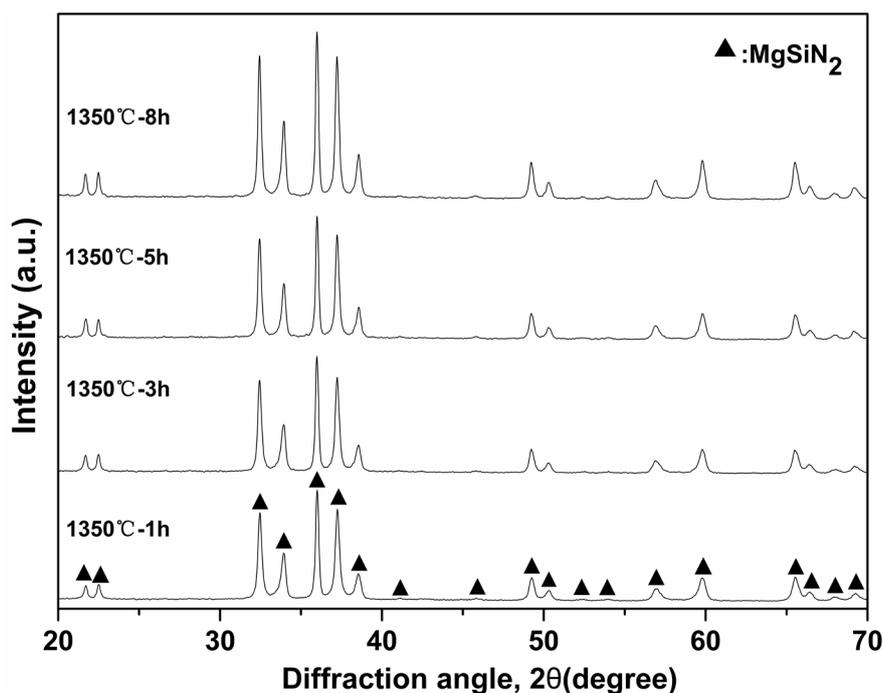


Figure 3. XRD patterns of the products synthesized at 1350°C after holding for different holding time.

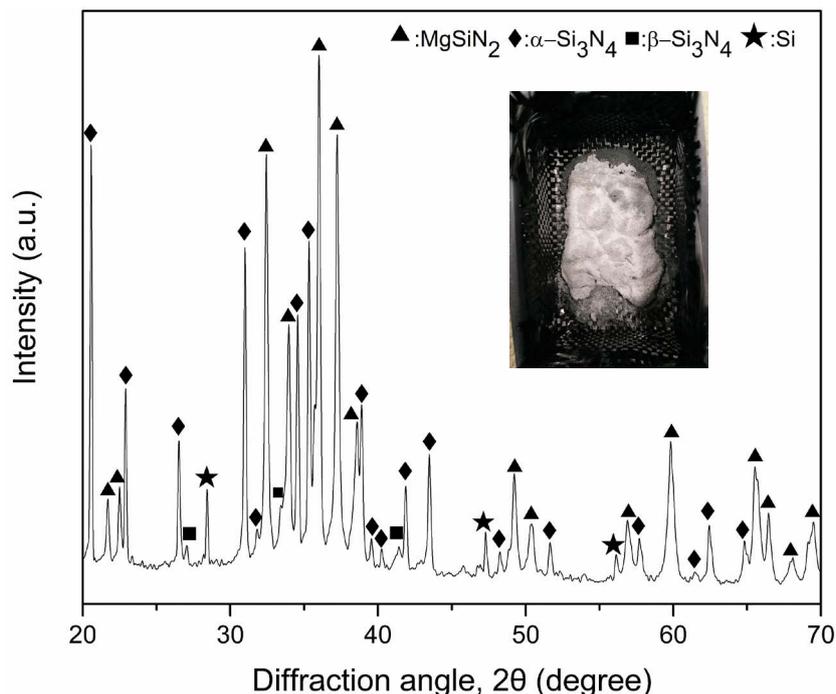


Figure 4. XRD pattern of the black powders surrounding the synthesized white products at 1350 °C after holding for 8 h.

Although the urea could reduce the Si content and produce smaller particles, a small amount of Si and MgO were found to be still present. Thus, we decided to increase the holding time in order to obtain single-phase MgSiN_2 and influence the morphology of the products. **Figure 5** shows the XRD patterns of the products synthesized at 1250 °C for different holding time. As the holding time increased, the Si impurity gradually decreased, and single-phase MgSiN_2 was obtained when the holding time was up to 11 h. By increasing the holding time, Si could be removed at low temperatures. **Figure 6** shows the SEM images and EDS patterns of the product synthesized at 1250 °C after holding for 5 h. The crystals mainly grew into two types, *i.e.*, lump and columnar. The EDS results of the sample are shown in the lower left corner of **Figure 6**, confirms that both types of products are MgSiN_2 . With the increase of the holding time, the grain size of the lumpy shaped crystals became larger. **Figure 7** shows the SEM images of the products synthesized at 1250 °C for (a) 8 h, (b) 1 h and at 1350 °C for (c) 1 h, while the diagrams on the right are partial enlargements of the left graphs. **Figure 7(b)** shows that the grains did not grow due to the low temperature and short time. As shown in **Figure 7(a)**, the grains gradually gathered and grew along the original column with the increase of the holding time. From **Figure 7(c)**, it is clear that when the temperature was high enough for the reaction to go to completion, the grains gradually sintered into blocks. In summary, with the increase of temperature and holding time, the particles gradually became larger; however, the temperature had a greater effect on the particle size than the holding time.

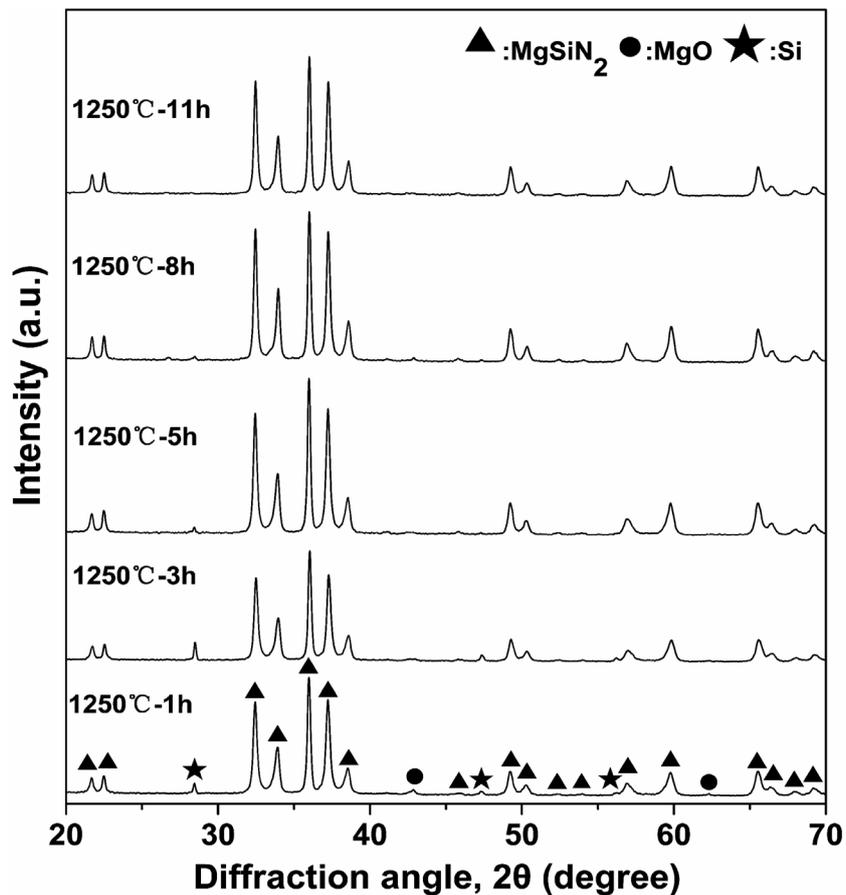


Figure 5. XRD patterns of the products synthesized at 1250°C for different holding times.

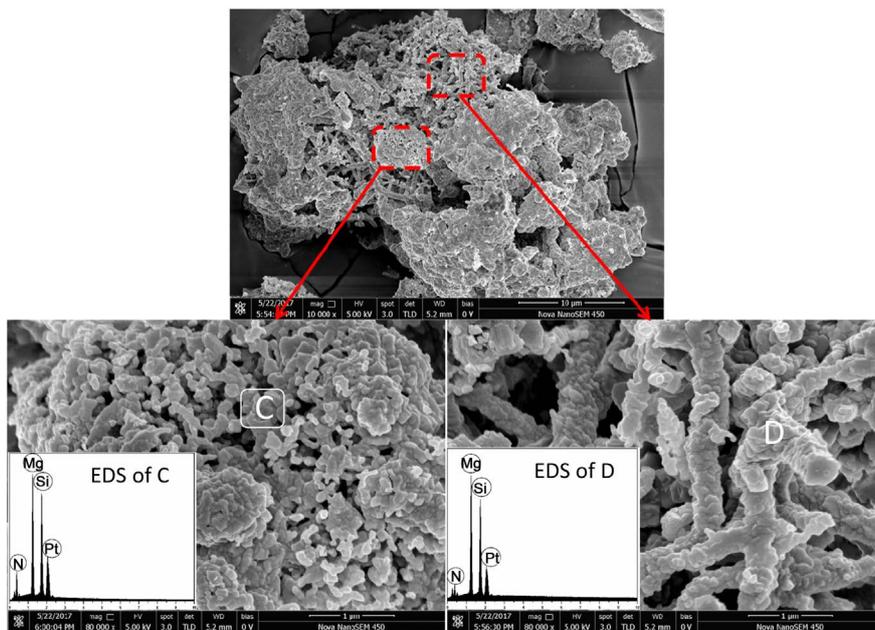


Figure 6. SEM images and EDS patterns of the product synthesized at 1250°C after holding for 5 h.

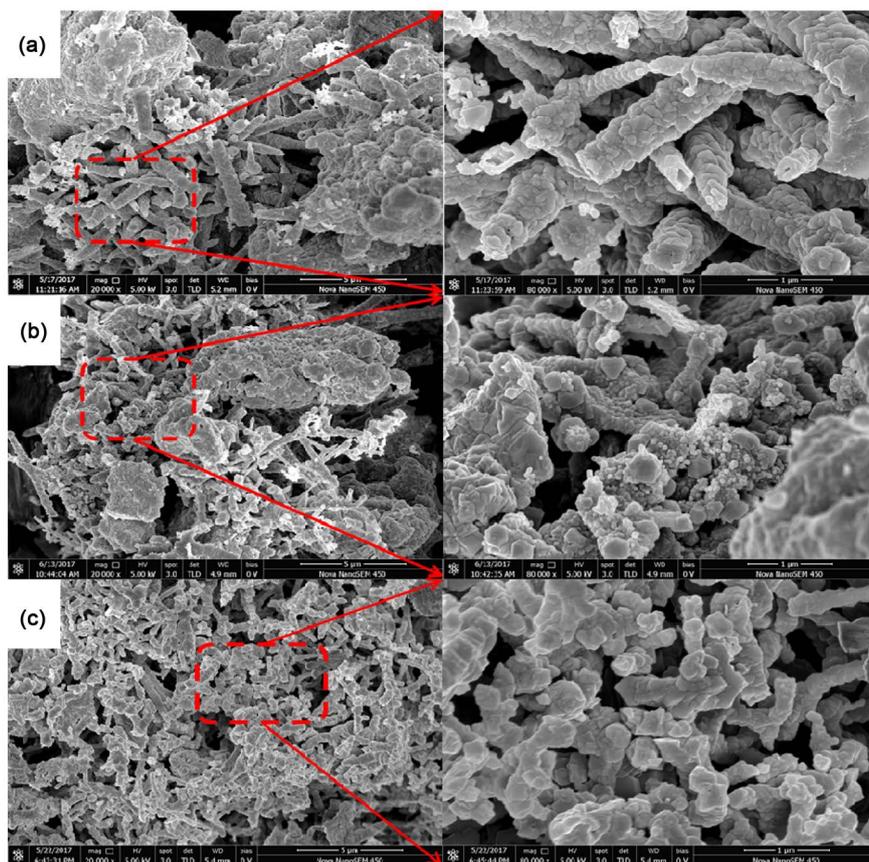


Figure 7. SEM images of the products synthesized at 1250°C after holding for (a) 8 h; (b) 1 h and at 1350°C for (c) 1 h.

From a large number of SEM photographs, it was evident that upon increasing of the holding time, the products with a columnar morphology gradually decreased at 1350°C. At 1250°C the products with a columnar morphology mostly appeared in a hollow, which may be caused by the evaporation of Mg. The formation of these voids also provides new space for the production of MgSiN_2 . Within a void, Mg and Si vapors may have a certain concentration gradient leading to the growth of many columns. Another form of growth is also shown in **Figure 8**. **Figure 8(a)** shows that the products with columnar morphologies grew on a solid surface. The columnar formation may be due to a larger temperature gradient on the solid surface. The farther away from the solid, the lower the temperature, the smaller the activity of the gas, and the easier it is to absorb the reaction gas; thus, MgSiN_2 easily grows along the tip. As shown in **Figure 8(b)**, it is possible that Mg and Si continued to grow along the inner surface of the cavity because of the relatively strong adsorption of nitrogen on the surface of Mg and Si. The schematic illustration of the mechanism of particle formation on solid surfaces and voids is shown in **Figure 9**. As the temperature increased, the reactants gradually reacted to form massive amounts of MgSiN_2 . However, the temperature was much higher than the boiling point of Mg, so a large amount of Mg and a small amount of Si evaporated. The evaporation of

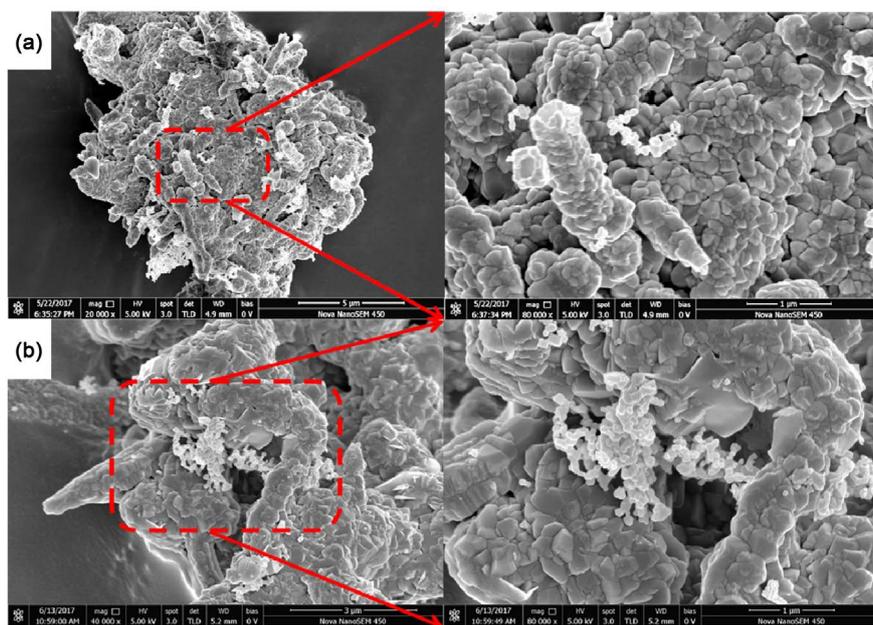


Figure 8. SEM images of the products synthesized at 1250 °C after holding for 8 h.

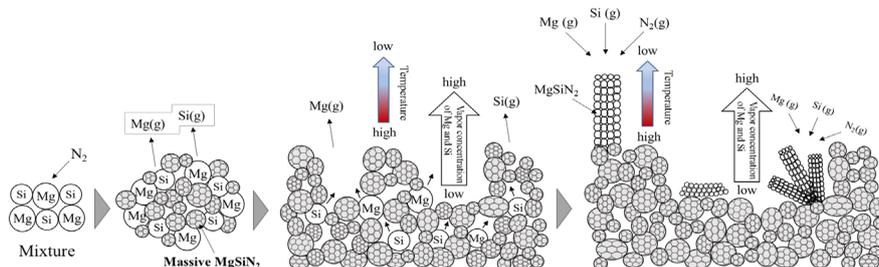


Figure 9. Schematic illustration of the mechanism of particle formation within solid surfaces and voids.

Mg and Si resulted in the formation of many voids in the blocky product. The higher is the temperature, the greater is the gas activity, and the smaller is the gas adsorption on the surface of MgSiN_2 [33]. This may be because the surface of block products possesses a certain temperature gradient. Thus, the farther away from the surface of the block product, the lower is the temperature, the more easily adsorbed is the gas; this promotes the growth of MgSiN_2 on the surface of massive products along the tip. Within the voids of the bulk products, it is possible that the evaporation of Mg and Si results in a concentration gradient of Mg and Si vapors in the void, resulting in the columnar growth of MgSiN_2 . However, it is possible that some of the surfaces of Mg and Si still have adsorption properties, which can absorb N_2 , Mg and Si atoms, so that some MgSiN_2 grows along the surface of the block products.

4. Conclusion

A single-phase of MgSiN_2 was obtained either at 1350 °C for 1 h or at 1250 °C for 11 h using Mg/Si as starting materials with a mole ratio of 2:1 under a N_2 at-

mosphere. Although this product could be obtained at low temperature (1250°C), the holding time required was too long and the process involved great energy consumption. Thus, the most economical temperature was 1350°C. With the increase of the holding time, the grain size of lumpy shaped crystals became larger, and the size of grains with a columnar morphology also increased becoming more uniform. As the temperature increased, the products with a columnar morphology gradually decreased. Moreover, when the temperature reached 1450°C, the decomposition of MgSiN₂ occurred, and Si₃N₄ particles could be clearly seen in the SEM images. This simple and energy-efficient method for the preparation of MgSiN₂ further promotes its use as a fundamental material for electronic equipment to achieve an enhanced thermal conductivity.

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