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Short communication

Preparation of single-phase magnesium silicon nitride powder by a two-step process

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Abstract

Single-phase magnesium silicon nitride ($MgSiN_2$) powder was prepared by a two-step process: combustion synthesis followed by acid washing. The effects of starting material compositions, diluent addition and N_2 pressure on the phase compositions of the final products were studied, and the acid washing process was also discussed. It is difficult to synthesize single-phase $MgSiN_2$ by one-stage combustion reaction through regulating the process parameters because of the evaporative loss of Mg. Combustion synthesis of $MgSiN_2$ by using an excess of magnesium in the starting materials and then acid washing off the impurity was an effective way to prepare the single-phase $MgSiN_2$ powder.

Keywords: Combustion synthesis; SHS; $MgSiN_2$; Diluent

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1. Introduction

$MgSiN_2$ is a ternary nitride with an orthorhombic crystal structure similar to that of aluminum nitride (AlN) [1]. Because of its excellent thermal conductivity which is comparable to that of AlN, great interest is focused on the fabrication of $MgSiN_2$. $MgSiN_2$ has been regarded as an suitable candidate to partly replace the relatively expensive AlN as a substrate of integrated circuits [2–5]. Also because of this property, $MgSiN_2$ has been successfully used as an effective sintering additive of high thermal-conductivity nitrogen ceramics. In addition, $MgSiN_2$ shows a high electric resistance at room temperature and rather good fracture toughness, strength and hardness, which makes it used as filler in resins or other polymers [3,6,7].

Recently, various methods have been developed to fabricate $MgSiN_2$ powders [5,8–12]. These processing routes, such as direct nitridation of Mg/Si or mixtures of binary nitrides, have no way to give a pure compound. Meanwhile, these synthesis processes usually require high-energy consumption due to the production circle. As a well-known technique for the preparation of a series of advanced materials, combustion synthesis (CS), also called self-propagating high-temperature synthesis (SHS), presents many advantages such as low processing cost, great energy efficiency, high purity of products and high production rate compared with conventional methods [13,14]. Thus, the synthesis of $MgSiN_2$ by combustion of several different starting materials (Mg/Si, Mg_2Si/Si_3N_4, Mg/Si_3N_4) was widely studied [5,6,9,15,16]. However, because Mg is easily evaporated from starting materials under the high combustion temperature, it is very difficult to fabricate single-phase $MgSiN_2$ powder through one-stage combustion synthesis. Therefore, a preparation of single-phase $MgSiN_2$ powder through combustion synthesis needs further study and discussion.

In this paper, $MgSiN_2$ powder with minor MgO content was prepared by combustion synthesis under the condition that Mg content was higher than the stoichiometric ratio in the starting materials. Then, single-phase $MgSiN_2$ powder was obtained through washing off the impurity using hydrochloric acid.

2. Experimental procedure

The starting materials used were: Mg (>99 wt.%, 74 μm, Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China) and Si_3N_4 (>99 wt.%, 0.79 μm, SN-E05, UBE

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Table 1
Starting material compositions and experiment conditions.

Sample	Composition, g	P_{N2}, MPa
	$Mg:Si_3N_4:MgSiN_2$	
S-1	34:66:0	0.5
S-2	34:66:0	1.0
S-3	34:66:0	5.0
S-4	39:66:0	0.5
S-5	39:66:0	1.0
S-6	43:66:0	1.0
S-7	34:66:10	1.0
S-8	34:66:20	1.0

Industries, Tokyo, Japan). The starting compositions were designed according to the following reaction Eq. (1), and the corresponding experiment conditions were shown in Table 1:

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

The raw materials were mixed for 2 h by agate balls in a plastic jar with absolute ethanol as medium. After ball milling, the obtained slurry was dried and sieved. Then, the reactant powder mixture was placed in a porous graphite crucible, and placed in the combustion reaction chamber. After evacuation, the reaction chamber was inflated with high-purity N_2 to a needing value. The combustion reaction was triggered by passing an electric current through a tungsten coil closely above the sample. The reaction temperature was measured by a W-R3/W-Re25 thermocouple, which was inserted into the center of the sample and connected with a computer system of data treatment.

The products were mechanically milled for 10 min using steel balls as the milling media. Then the powders were stirring in the hydrochloric acid (3.0 mol/L) for 120 min with 80 °C water bath. The obtained slurry was filtered and washed with distilled water for 6–8 times. The filter cake was dried and milled.

The phase composition was determined by X-ray diffraction (XRD; Cu Kα, Rigaku, Japan) and the microstructure was observed by scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan) equipped with energy dispersive spectroscopy detector (EDS; INCA, Oxford Instrument).

3. Results and discussion

3.1. Preparation of $MgSiN_2$ powder by combustion synthesis

Fig. 1 shows the temperature curves of the sample S-2 during the combustion synthesis process. It can be seen that the temperature sharply increases to the apex of 2170 °C in only several seconds, and then begins to decrease. It nearly holds about 254 s above 1090 °C which is the boiling point of Mg. The combustion velocity (V_c) is about 2.5 mm/s. The X-ray diffraction (XRD) pattern of the sample S-2 is shown in Fig. 2. The result shows that the dominant phase of the combustion product is $MgSiN_2$, and a small amount of Si_3N_4 is found in it. The reason may be that Mg is evaporated from the starting materials due to the combustion temperature sharply increases above the boiling point of Mg and lasts for a long time. So the value of Mg/Si_3N_4 deviates from the stoichiometric ratio during the combustion process, and the residual Si_3N_4 is present in the product. Therefore, the single-phase $MgSiN_2$ could not be synthesized by combustion of the stoichiometric ratio of Mg/Si_3N_4 in starting materials.

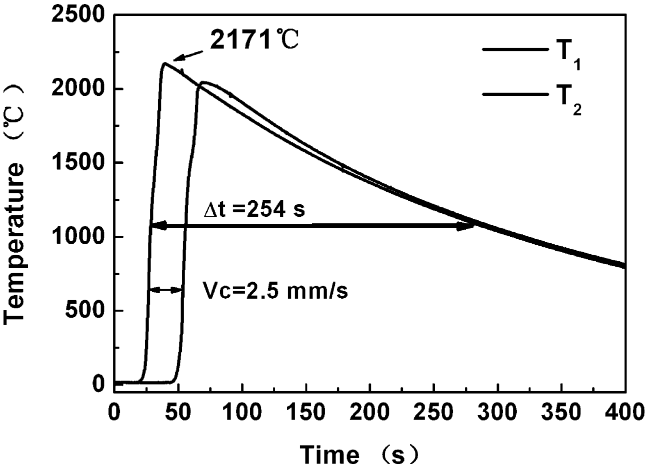

Fig. 1. Temperature variation curves of sample S-2 during the combustion synthesis process.

3.1.1. Effects of the Mg content on the phase compositions of combustion synthesis products

Fig. 3 shows the XRD patterns of the combustion products fabricated by starting materials with different amounts of Mg powder. It is found that $MgSiN_2$ and Si_3N_4 are present in the product of S-2 which contains the stoichiometric content of Mg. However, products of S-5 and S-6 in which Mg content separately was 5 wt.% and 10 wt.% higher than the stoichiometric value together contain $MgSiN_2$ and MgO. In both of S-5 and S-6, enough Mg powder made all of starting Si_3N_4 powders engage in the reaction, and the rest Mg could react with N_2, whose products were Mg_3N_2. Due to the easily and rapidly hydrolyzation and oxidization of Mg_3N_2, the formation MgO

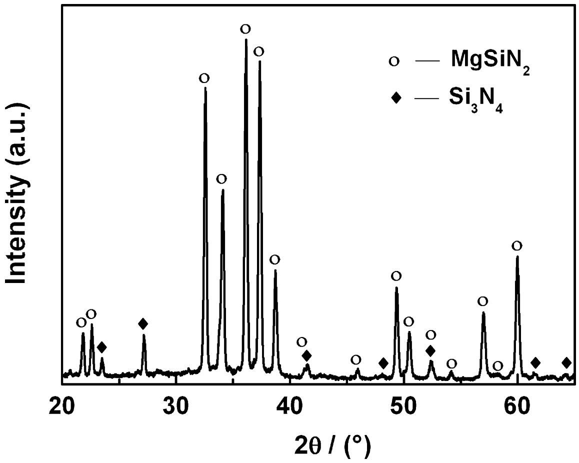

Fig. 2. X-ray diffraction (XRD) pattern of the combustion product of sample S-2.

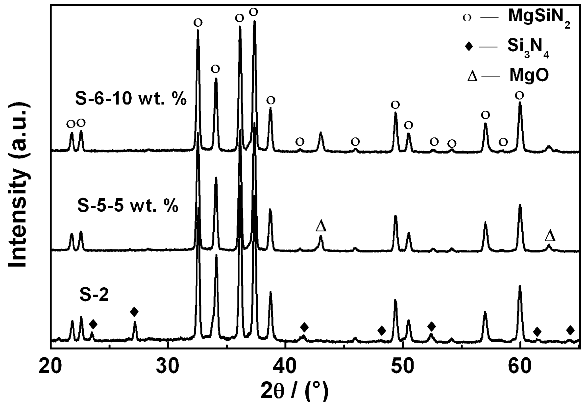

Fig. 3. XRD patterns of the combustion products synthesized by starting materials with different amounts of Mg.

was found in the final combustion product. Additionally, the formation of MgO may partly be derived from the oxygen impurities in the starting materials (oxygen and/or water vapor adsorbed on the surfaces of starting Mg particles) and oxygen pickup during the processing (mixing) and the synthesis (oxygen impurities in the N_2 atmosphere) [5,16].

3.1.2. Effects of diluent content on the phase compositions of combustion synthesis products

The XRD patterns of the combustion products synthesized by starting materials with different amounts of $MgSiN_2$ diluent are shown in Fig. 4. We can see that products of S-7 and S-8, separately including 10 wt.% and 20 wt.% $MgSiN_2$ diluent in the starting materials, both contain $MgSiN_2$, Si_3N_4 and MgO, which is different from that of sample S-2. The diluent was used to control the temperature of the reaction and to reduce the evaporation of Mg, as well as to enhance the infiltration of N_2 [17–19]. It is not effective to reduce the loss of Mg vapor by adding diluent in starting materials even the content of diluent is as high as 20 wt.%. So the unreacted Si_3N_4 can also be found in the products of S-7 and S-8.

3.1.3. Effects of nitrogen pressure on the phase compositions of combustion synthesis products

Fig. 5 shows the XRD patterns of the products synthesized at different N_2 pressure levels with the stoichiometric ratio of starting materials. It can be seen that $MgSiN_2$ is the major phase in these products as the N_2 pressure decreases from 5.0 MPa to 0.5 MPa. Theoretically, the combustion temperature will go down with the decreasing of the N_2 pressure, which would reduce the evaporation of Mg to some degree. However, it was not remarkable to reduce the loss of Mg vapor even the N_2 pressure was as low as 0.5 MPa. Consequently, Si_3N_4 cannot be completely consumed during the combustion synthesis just by adjusting the pressure.

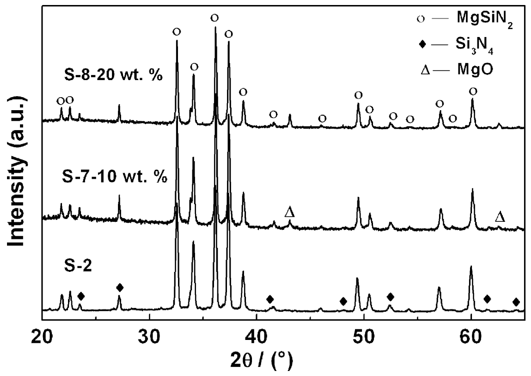

Fig. 4. XRD patterns of the combustion products synthesized by starting materials with different amounts of diluent.

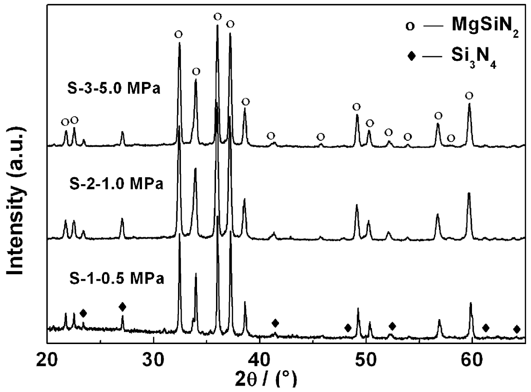

Fig. 5. XRD patterns of the combustion products synthesized under different N_2 pressures.

3.2. Effects of acid washing on the phase compositions of combustion synthesis products

Fig. 6 shows the XRD patterns of the S-5 products before and after acid washing, respectively. It can be seen that there are $MgSiN_2$ and MgO in the product which is not washed with hydrochloric acid. But after acid washing, only one phase, $MgSiN_2$, is present in the sample. It suggests that MgO is washed off clearly.

Water bath with 80 °C can enhance the reaction activities during the acid washing process, so it is beneficial to remove the impurities clearly. Therefore, for the combustion products only containing minor MgO impurity, it is a sample method to obtain single-phase $MgSiN_2$ powder through acid washing.

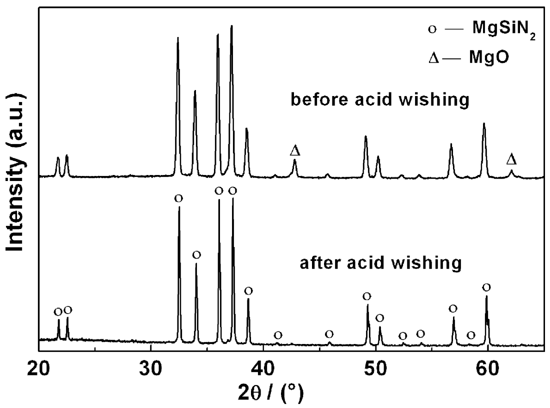

Fig. 6. XRD patterns of the sample S-5 before and after acid washing.

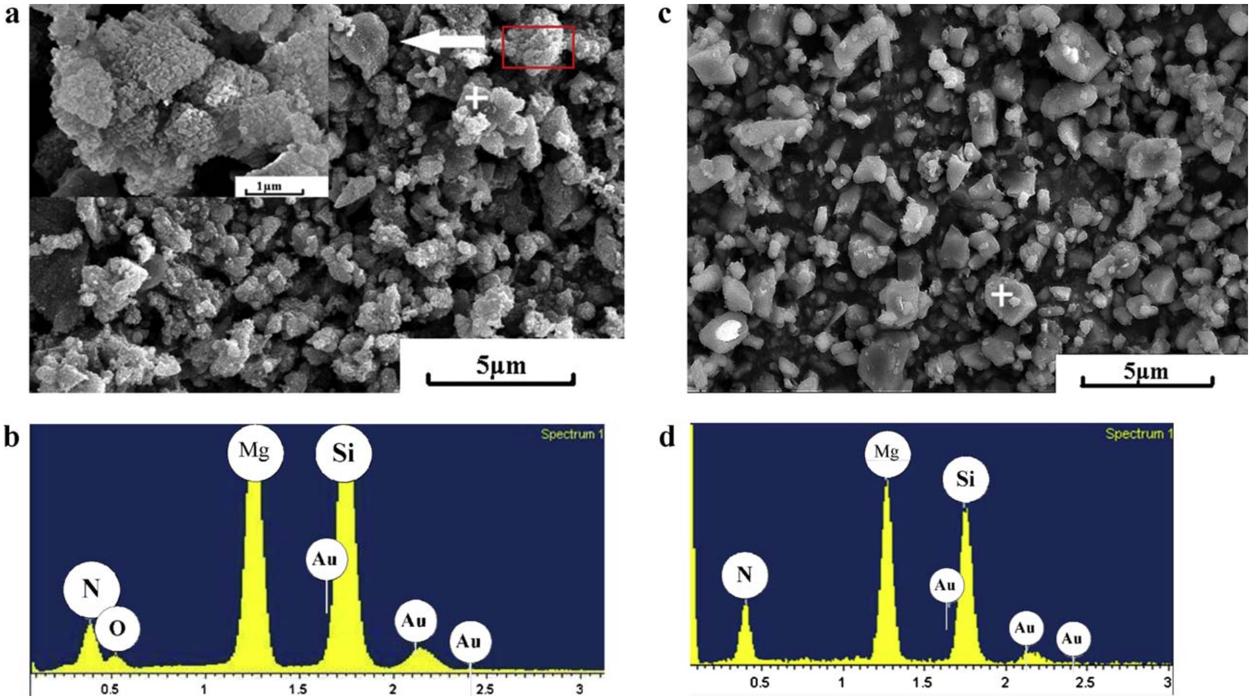

Fig. 7. Scanning electron microscope (SEM) photographs and EDS analysis results of the sample S-5 before (a and b) and after acid washing (c and d).

3.3. *Characteristics of combustion products and single-phase $MgSiN_2$ powder*

The SEM images and EDS analysis results of the sample S-5 before and after acid washing are shown in Fig. 7. The combustion product mainly consists of grains with different sizes, and there is an obvious agglomeration between grains, as shown in Fig. 7(a). The inset image of Fig. 7(a) shows that the surface of grains is coarse with many smaller submicron grains. The EDS result of the same sample, as shown in Fig. 7(b), confirms that there are $MgSiN_2$ and MgO in the product. However, after acid washing, the surface of grains becomes smooth and the non-uniform particle size is blow 3 μm, as shown in Fig. 7(c). The EDS result of this sample, as shown in Fig. 7(d), indicates that the powder only includes $MgSiN_2$ grains.

From the above results, we can find that in the product directly fabricated by combustion synthesis, $MgSiN_2$ grains are wrapped with finer MgO grains. But through the simple hydrochloric acid washing, MgO can be effectively removed and single-phase $MgSiN_2$ powder can be obtained.

4. Conclusion

Under high N_2 pressure, combustion synthesis could be achieved using Mg/Si_3N_4 as reactants, and the products were powders with $MgSiN_2$ as the major phase. Because the combustion temperature was much higher than the boiling point of Mg and the last time above the high temperature was very long, the loss of Mg by evaporation was very serious. As a result, the combustion synthesis reaction deviates from the stoichiometric ratio, and residual Si_3N_4 was found in the products. Through adding excess content of Mg to complement the loss of Mg evaporation, adding diluent and decreasing N_2 pressure, single-phase $MgSiN_2$ powder could not be obtained directly by one step of combustion synthesis. $MgSiN_2$ powder with low level of MgO impurity was synthesized by adding excess content of 5 wt.% Mg in the starting materials. Through a simple and effective hydrochloric acid washing process with 80 °C water bath, MgO can be removed and single-phase $MgSiN_2$ powder was obtained with well-dispersed grains.

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References

[1] C.M. Fang, et al., *Ab initio* band structure calculations of Mg_3N_2 and $MgSiN_2$, J. Phys.: Condens. Matter 11 (1999) 4833–4842.
[2] S. Tanaka, K. Itatani, H.T. Hintzen, Effect of silicon nitride addition on the thermal and mechanical properties of magnesium silicon nitride ceramics, J. Eur. Ceram. Soc. 24 (2004) 2163–2168.
[3] W.A. Groen, M.J. Kraan, Preparation, microstructure and properties of $MgSiN_2$ ceramics, J. Eur. Ceram. Soc. 12 (1993) 413–420.
[4] G.H. Peng, et al., Spark plasma sintered silicon nitride ceramics with high thermal conductivity using $MgSiN_2$ as additives, J. Am. Ceram. Soc. 92 (9) (2009) 2122–2124.
[5] H. Uchida, et al., Synthesis of magnesium silicon nitride by the nitridation of powders in the magnesium–silicon system, J. Ceram. Soc. Jpn. 105 (11) (1997) 934–939.

[6] F. Wang, Combustion synthesis of $MgSiN_2$ powders using urea as additives, Rare Metal Mater. Eng. 37 (1) (2008) 505–508.
[7] G.H. Peng, et al., Fabrication of β-Si_3N_4 Whiskers by combustion synthesis with $MgSiN_2$ as additives, Mater. Res. Bull. 40 (2005) 2139–2143.
[8] L. Peng, et al., Large-scale synthesis of magnesium silicon nitride powders at low temperature, J. Am. Ceram. Soc. 91 (1) (2008) 333–336.
[9] Z. Lenoes, K. Hirao, Y. Yamauchi, S. Kanzaki, Reaction synthesis of magnesium silicon nitride powder, J. Am. Ceram. Soc. 86 (7) (2003) 1088–1093.
[10] F.F. Grekov, B.V. Chernovets, Methods for $MgSiN_2$ synthesis, Russ. J. Appl. Chem. 77 (2004) 1223–1226.
[11] A. Anderson, R.B. Kaner, A Solid-state metathesis route to $MgSiN_2$, Chem. Mater. 17 (2005) 2155–2161.
[12] R.G. Blair, A.A. Kudyba-Jansen, P. Gerharts, H.T. Hintzen, R. Metselaar, Preparation, characterization and properties of $MgSiN_2$ ceramics, J. Mater. Sci.: Mater. Electron. 13 (2002) 63–75.
[13] A.G. Merzhanov, I.P. Borovinskaya, Self-propagating high-temperature synthesis of refractory inorganic compounds, Doklady Akademii Nauk SSSR 204 (2) (1972) 366–369.
[14] G.H. Liu, et al., Fast shape evolution of TiN microcrystals in combustion synthesis, Cryst. Growth Des. 6 (10) (2006) 2404–2411.
[15] G.H. Peng, et al., A novel route for preparing $MgSiN_2$ powder by combustion synthesis, Mater. Sci. Eng. A 397 (2005) 65–68.
[16] R.J. Bruls, H.T. Hintzen, R. Metselaar, Preparation and characterisation of $MgSiN_2$ powders, J. Mater. Sci. 34 (1999) 4519–4531.
[17] K. Hirao, Y. Miyamoto, M. Koizumi, Combustion reaction characteristics in the nitridation of silicon, Adv. Ceram. Mater. 2 (4) (1987) 780–783.
[18] I.G. Cano, et al., Self-propagating high temperature-synthesis of Si_3N_4: role of ammonium salt addition, J. Eur. Ceram. Soc. 21 (3) (2001) 291–295.
[19] I.G. Cano, I.P. Borovinskaya, M.A. Rodriguez, V.V. Grachev, Effect of dilution and porosity on self-propagating high-temperature synthesis of silicon nitride, J. Am. Ceram. Soc. 85 (9) (2002) 2209–2211.