

Preparation of Si₃N₄ powder by combustion synthesis

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The present paper addresses a possible route for the manufacturing of silicon nitride (Si₃N₄) powder under rather a low pressure of nitrogen using a combustion synthesis (CS) method. Reactant mixtures were diluted by 30-50 wt% of Si₃N₄ to avoid the melting of silicon during combustion. Si₃N₄ powders with $\alpha/(\alpha + \beta)$ ratios were prepared in a loose powder mixture state in the temperature range of 1500-2200 °C with dwell times from 10 to 60 minutes. The influence of the amount of ammonium fluoride (NH₄F) in the mixture with silicon, the silicon particle size distribution, and the nitrogen pressure on the extent of silicon conversion into silicon nitride was experimentally studied. It was revealed that a small ammonium fluoride addition to silicon powder allowed the production of silicon nitride powder with a good output for industrialization. Because of the existence of the NH₄F, the reaction involves not only the silicon nitriding mechanism, the growth of α -Si₃N₄ occurred partially by a vapor-crystal growth mechanism, and a vapor-liquid-solid (VLS) mechanism works during the rod-like β -Si₃N₄ growth. The as-synthesized samples were characterized using X-ray diffraction and scanning electron microscopy analyses. Possible mechanisms of CS Si₃N₄ particle growth are discussed. CS technology has the advantage over traditional technology in simple equipments, low cost, high quality and relative good sintering activity.

Key words: Combustion Synthesis, α -Si₃N₄, β -Si₃N₄.

Introduction

Highly developed-ceramic materials based on silicon nitride require extremely pure and well-characterized starting powders. The starting powder determines the sintering behavior and the subsequent microstructural formation. Hence, the resulting material properties depend to a large extent on the starting powders and the technique of their manufacture. One can obtain a wide variety of strength versus temperature, creep and oxidation behavior depending on the purity and phase composition of the starting silicon nitride powders. The main obstacle for a wider use of Si₃N₄-based materials is the cost of their synthesis and final processing. Direct silicon nitridation, carbothermal reduction, a vapor phase reaction and thermal decomposition are the most commonly used processes. These synthesis techniques usually require high energy contributions during long periods of time and the production rates are very low, hence, the high production cost.

Combustion synthesis (acronym: CS), or the so-called self-propagating high-temperature synthesis (acronym: SHS), originally developed in the former USSR, whereby the heat generated by an exothermic reaction sustains the reaction itself along a combustion wave after external ignition, attracts an increasing interest for producing many materials. With regard to Si₃N₄ synthesis, CS has been successfully applied in a pressurized nitrogen atmosphere. Compared with the conventional synthesis methods of Si₃N₄, the CS technique

presents large advantages such as great energy efficiency, high purity of the products and high production efficiency [1]. As was previously described [2], the combustion of Si₃N₄ in a nitrogen atmosphere presents a high reaction speed and, therefore, the microstructure is difficult to control. Besides, the combustion temperatures are very high and silicon particles melt in the combustion front and coalesce during the reaction, which inhibits complete nitridation. The kinetics of Si combustion in a pressurized nitrogen atmosphere is fast and the combustion temperature ($T > 1500$ °C) at the combustion front is far higher than the melting point of Si. Melting and coalescence of Si can inhibit complete Si nitridation. Si₃N₄ powder is usually mixed into the initial mixture as a diluent to suppress such a problem, while ammonium salts are added in the initial mixture (generally ammonium halides, such as NH₄Cl and NH₄F) to control the nitridation reaction [3]. Most of the researches agree that mainly Si₃N₄ with a high β -phase content is formed during the silicon nitridation by CS, however, a final product rich in α -Si₃N₄ is rather desirable. Some studies have successfully tackled this problem reporting the fabrication of a product rich in α -Si₃N₄ by CS at a nitrogen pressure of 3-10 MPa [4, 5]. This study, under the perspective of technology also discussed the influence and the impact of Si powder on the CS of Si₃N₄.

Experimental

The reactions have been performed in a stainless steel CS reactor with a 30l volume capacity and a 900 mm useful length. The following starting materials have been used:

(1) Silicon powder with 99.5 wt% purity and Fe < 0.3 wt% and Al < 0.1 wt%, Ca < 0.05%;

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(2) Self-made Si_3N_4 powders obtained by CS as diluents and the following composition: α -phase > 93wt%, Fe < 0.06 wt%, C < 0.1 wt%;

The particle size distributions of the original silicon and Si_3N_4 powders are listed in Table 1;

(3) NH_4F (Beijing Chemical Co., Beijing, China) with 99.5 wt% purity;

(4) Nitrogen with 99.99%, O_2 < 2 ppm; C_nH_m < 0.1 ppm; CO < 0.5 ppm; H_2 < 1 ppm.

Powder mixtures with a weight $\text{Si}/\text{Si}_3\text{N}_4/\text{NH}_4\text{F}$ proportion of 42.5/47.5/9 were milled using Si_3N_4 balls as the milling media with a ball/charge weight ratio of 10 : 1 for 1 hour. The composition and combustion conditions of CS samples are listed in Table 2. The milled powders were then sieved through a 40 mesh screen and loosely packed in a porous graphite crucible which was 50 mm in diameter and 800 mm in length. The porosity of the green mixture was about 70-80%. A single load in the crucible was 2000 g. The crucible was then placed in the CS reactor. The hermetically sealed reactor was evacuated to a vacuum of 10^{-4} MPa and then filled with high-purity N_2 to a desired pressure. The ignition was initiated in one extreme of the reactor using a W electrical resistor which was buried within a mixture of Ti : C 1/1 mol%.

The combustion temperature was recorded with a W-Re3/W-Re25 thermocouple (0.5 mm in diameter) inserted into the center of the starting mixtures. The content of crystalline phases was determined with X-ray diffraction (XRD)

Table 1. Particle size distribution of silicon and silicon nitride powders

Sample No	D10 (μm)	D50 (μm)	D90 (μm)	Fe	Purity
Si_3N_4	0.205	3.07	12.28	0.06%	99.64%
Si-1	0.27	2.02	5.42	0.237%	99.7%
Si-2	0.35	4.02	8.78	0.252%	99.7%
Si-3	0.46	5.96	11.09	0.243%	99.7%
Si-4	0.59	8.03	15.78	0.248%	99.7%

Table 2. Composition and combustion condition of CS samples

Sample No	Si_3N_4 (wt%)	Si (wt%)	NH_4F (wt%)	Nitrogen Pressure (MPa)
CS 1	47.5	42.5(Si-1)	9	3
CS2	47.5	42.5(Si-1)	9	5
CS3	47.5	42.5(Si-1)	9	8
CS4	47.5	42.5(Si-2)	9	5
CS5	47.5	42.5(Si-3)	9	5
CS6	47.5	42.5(Si-4)	9	5

Table 3. Combustion result of CS samples under different nitrogen pressures

Sample No	Maximum Temperature ($^{\circ}\text{C}$)	Maximum pressure (MPa)	Dwell time (minutes)	Combustion velocity (mm/s)	Particle size distribution			
					D10 (μm)	D50 (μm)	D90 (μm)	Sp (m^2/g)
CS 1	1510	7.5	42	0.16	0.234	3.29	11.45	4.93
CS2	1740	12.3	34	0.20	0.224	5.26	16.03	3.50
CS3	2049	15.9	28	0.24	0.386	9.08	22.05	2.95

analysis (Rigaku Geigerflex D/Max, C Series, Cu $K\alpha$ radiation Japan), the proportion of Si_3N_4 phases were calculated according to the Gazzara and Messier method [6]. The morphologies of the as-synthesized products were observed on the fracture surfaces by scanning electron microscopy (JEOL, JSM-5610LV). For comparative purposes, a laser diffraction particle size analyzer (Mastersizer2000 Model S, Malvern Instruments, U.K) was used. The specific surface area of the as-prepared powder was measured by the BET method with a Flow Sorb ST-03 equipment.

Results and Discussion

The effect of nitrogen pressure

Considering that the reactants powder compact of reactants is a porous body, synthesis of Si_3N_4 was carried out at pressures ranging from 3 to 8 MPa, CS1 and CS2 products had a grey, loose and friable character, while the CS3 product had the right character, hard to crush, and no black powder was found in the three samples. Combustion temperatures (the maximum temperature), particle size distribution, the maximum pressures reached during the processes, dwell time, and combustion velocity of sample CS1, CS2 and CS3 are listed in Table 3. It is obvious that the combustion temperature, combustion velocity, maximum pressure, particle size and β -phase content increased with an increase in the nitrogen pressure, while the specific surface area decreased. Fig. 1 shows the X-ray

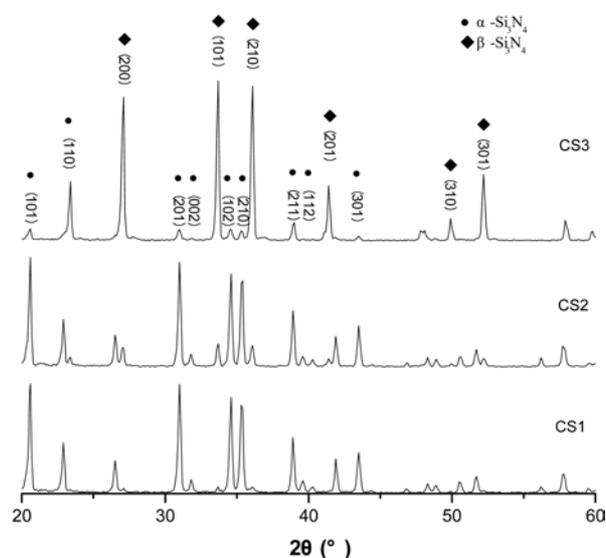


Fig. 1. X-ray diffraction patterns of samples formed with different initial nitrogen pressures.

powder diffraction patterns of the samples. The final products contain only the Si_3N_4 phase and no diffraction peaks due to residual Si were found in the XRD patterns, which indicates that the Si powders have been fully nitrated. They also indicate that an increase in the nitrogen pressure stimulates an increase in the combustion temperature, thus leading to an increase in the β -phase content and combustion velocity. According to the results of the intensity of X-ray diffraction peaks, the percentages of CS1, CS2, CS3 were 96%, 89%, 3.6% respectively. It is obvious that some α - Si_3N_4 added in the CS2 and CS3 samples was converted to β - Si_3N_4 during combustion. It was unavoidable that some α - Si_3N_4 dilution was converted to β - Si_3N_4 during

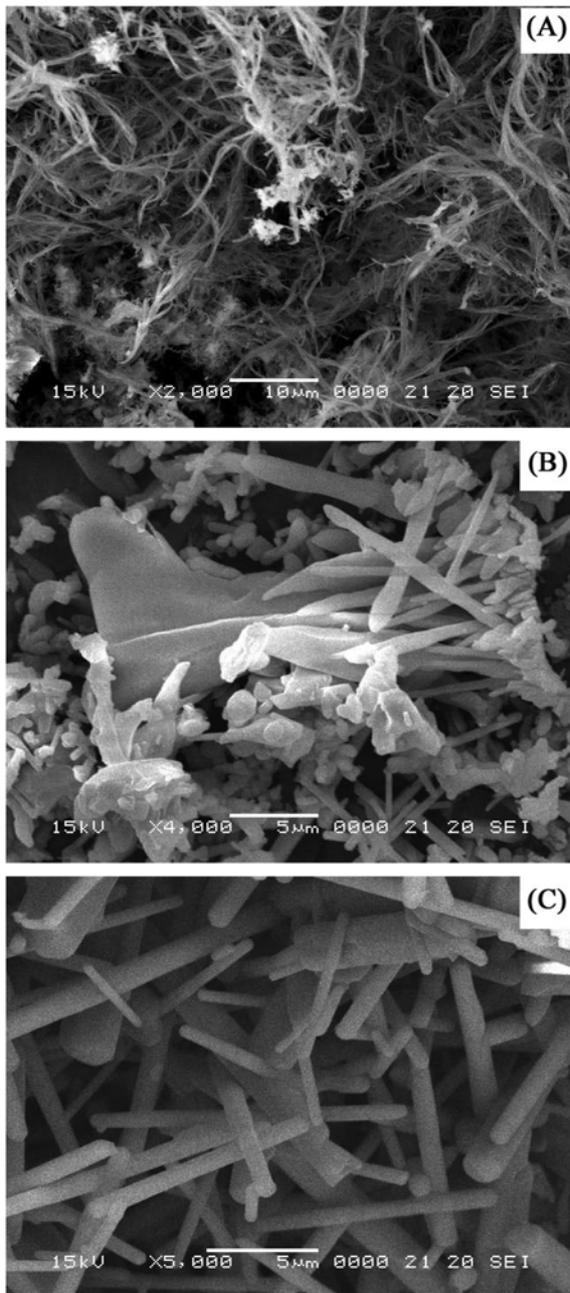


Fig. 2. Scanning electron micrographs of Si_3N_4 formed under different nitrogen pressures: (A) CS1, (B) CS2, (C) CS3.

combustion, it is generally argued that the α phase, mainly in powder form, may transform to the β phase by a solution-precipitation mechanism [7]. The conversion ratio of $\alpha \rightarrow \beta$ was promoted by increasing the initial nitrogen pressure.

Fig. 2 are scanning electron microscopy (SEM) images of sample CS1, 2, 3. We can see that CS1 (mainly α -phase) is composed of twisted dendritic fibers, while CS3 is composed of straight rod-like fibers with a length in the range of 5 to 100 μm and diameters of about 0.3–4 μm , CS2 is mostly composed of curvulate fibers with some anomalous particles. Almost every crystal of CS3 had a round tip, which indicated the VLS (vapor-liquid-solid) mechanism played a main role [8]. With an increase of initial N_2 pressure, the combustion temperature increases, and Si_3N_4 crystals grow completely.

The effect of the silicon particle size distribution

Powders of an average particle size from 2–8 μm were used in the study of the effect of the silicon particle size on the synthesis parameters and the final product properties. The initial particle size of the powders used exerted a strong effect on the synthesis parameters and the characteristics of the final products. A variation of the fractional composition of the silicon powder caused changes in the synthesis temperature, α -phase content, particle size and the combustion velocity. It can be seen that an increase in the silicon particle diameter is accompanied by a decrease in the specific surface area of the Si_3N_4 and an elevation of the combustion temperature. A significant effect of the synthesis temperature on the specific surface area of Si_3N_4 is particularly noticeable at low temperatures (1400–1750 $^\circ\text{C}$). The combustion velocity is a response of the extent of the reaction. The finer the silicon particle size, the higher the β -phase content, the higher the combustion temperature, the larger the product particle size, and the lower the specific surface area. From Fig. 3 and Table 4 we can see that sample CS6 with 95.7% α -phase, $T = 1560$ $^\circ\text{C}$, $S_p = 4.50$ m^2/g , CS5 with

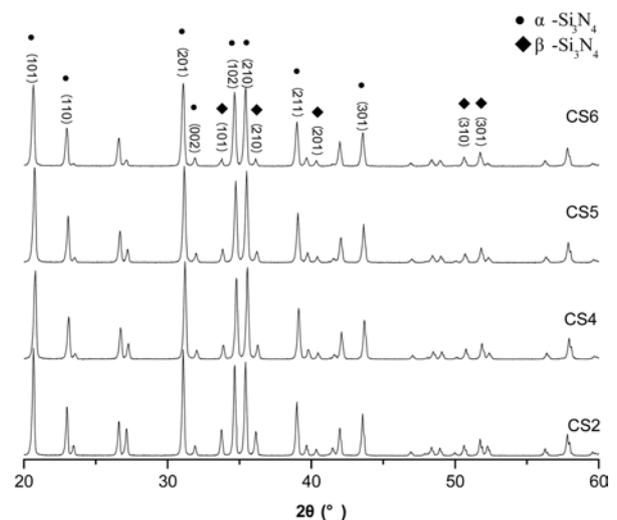


Fig. 3. X-ray diffraction patterns of product synthesized with silicon with different particle sizes.

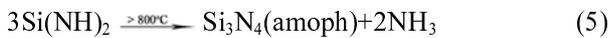
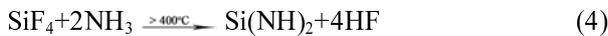
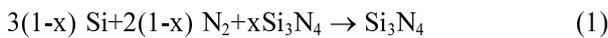
Table 4. Combustion results of CS samples synthesized with different silicon particle sizes

Sample No	Maximum Temperature (°C)	Maximum pressure (MPa)	Dwell time (minutes)	Combustion velocity (mm/s)	Particle size distribution			
					D10	D50	D90	S _{sp}
CS2	1710	12.3	34	0.20	0.22	5.26	16.03	3.50
CS4	1660	11.5	39	0.17	0.20	4.60	14.90	3.76
CS5	1608	11.1	44	0.15	0.20	3.78	12.54	4.07
CS6	1560	10.7	50	0.13	0.18	2.93	11.05	4.50

93.2% α -phase, T = 1608 °C, Sp = 4.07 m²/g, CS4 with 89.3% α -phase, T = 1660 °C, Sp = 3.76 m²/g.

Growth mechanism of Si₃N₄ particles

As is known from early studies on the CS of Si₃N₄, that the adiabatic combustion temperature for the Si-N₂ reaction is higher than the melting point of Si (1693 K) and may also be higher than the dissociation temperature of Si₃N₄ [9]. When the temperature for Si melting is reached, Si powders cannot be completely nitrided. The addition of diluents into the reactants has been proved to be an effective way of preventing the coalescence of molten Si particles, it also brings a suitable porosity of the reactant with a stable compatible solid surface, which allows higher conversion to be achieved as a result of molten silicon spreading and being exposed to N₂ to react to Si₃N₄ [10]. Within this process, NH₄F played an important role in preventing the coalescence of molten Si particles during the combustion process. In other words, the addition of the low cost NH₄F additive to the Si powder reactants has the same effect with respect to controlling the maximum combustion temperature as does the Si₃N₄ diluent. Other ammonium salt additives, such as NH₄Cl, (NH₄)₂CO etc, also have strong influence on the CS reaction [11-13]. The total reaction schemes are as follows:



As can be seen from above reactions, the total thermal effect of silicon nitriding is insufficient for the self-sustaining process, it is obvious that the driving force of the process

is reaction (1). Within this process, NH₄F was added, when heated, it decomposed to NH₃ and HF and consumed some thermal energy from the reaction environment [14], increasing the concentration of N₂ inside the reacting mixture. Meanwhile, the decomposition of NH₄F lowered the combustion temperature due to the endothermic character of this reaction, thus offering a good way to control the reaction temperature. Reaction (2) begins in the heating zone of the green mixture at T > 150 °C, reaction 3 is initiated at T > 300 °C or higher temperatures. Silicon tetrafluoride enters into an immediate interaction with ammonia to form silicon imide, for the high combustion temperature, the unstable silicon imide decomposes to amorphous silicon nitride at T > 1000 °C, when the combustion temperature reaches to 1200 °C or higher, amorphous silicon nitride begins to convert to α -Si₃N₄. From the XRD analysis, CS 1 is mainly composed of the α phase, and the combustion temperature is not high enough to activate reaction 7, reaction 1, 6, 8 play predominant roles during α -Si₃N₄ formation, the vapor-crystal growth mechanism favors the formation of α -Si₃N₄, as for CS3, nearly 100% β -Si₃N₄ was obtained, and the combustion temperature reached higher than 2000 °C, nearly all the above reactions worked during the synthesis of rod-like β -Si₃N₄, Si_{sol}, Si_{liq}, and Si_{gas} reacted with the nitrogen resource to form β -Si₃N₄, which agrees fairly well with Mukasyan's results [15], the VLS mechanism should be considered as the most important growth mechanism with SHS of β -Si₃N₄.

Conclusions

The method studied in this article was both efficient and low-cost. It allowed α -Si₃N₄ powders to be obtained with desired the α -phase content by varying processing parameters. With an initial nitrogen pressure increase, the β -phase content, particle size, combustion velocity and maximum temperature of the reaction increased simultaneously. When the initial nitrogen pressure was about 8 MPa, the final product was inclined to strait rod-like β -Si₃N₄ fibers. Also, the initial silicon particle size distribution played a fairly important role during the synthesis, fine silicon powder was apt to synthesize high β -phase content powders with small surface areas.

High percentages of Si₃N₄ were obtained with the addition of NH₄F. The addition of salts to the raw material mixture plays a predominant role in the reaction, which affects

the presence of phases and their contents. Because of the existence of the NH_4F , the reaction involves not only the silicon nitriding mechanism, the growth of $\alpha\text{-Si}_3\text{N}_4$ occurred partially by a vapor-crystal growth, and the vapor-liquid-solid mechanism works during the rod-like $\beta\text{-Si}_3\text{N}_4$ growth.

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