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Carbothermal reduction and nitridation synthesis of silicon nitride by using solution combustion synthesized precursors

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Abstract Carbothermal reduction and nitridation synthesis of Si_3N_4 was investigated by using precursor powders prepared by a solution combustion synthesis method. Glycine or urea (fuel), ammonium nitrate (oxidizer), silicic acid (Si source), and sucrose (major carbon source) were dissolved completely in water. This solution was dried and then heated to undergo the solution combustion synthesis reaction, resulting in a homogeneous mixture of nano-sized carbon and SiO_2 particles, which was used as the precursor powder for the carbothermal reduction and nitridation synthesis of Si_3N_4. When the carbothermal reduction and nitridation reaction was carried out at 1,425–1,450 °C for 4 h, formation of Si_3N_4 can be detected only when the C/SiO_2 weight ratio is greater than $\sim$2.0. The Si_3N_4 yield increases rapidly as the C/SiO_2 weight ratio is increased from $\sim$2.0 to 2.8 and decreases with further increase in the C/SiO_2 ratio. The α-phase content increases with increasing C/SiO_2 weight ratio and decreases with increasing temperature. Depending on the C/SiO_2 ratio, a Si_3N_4 yield of $\sim$80 wt% and an α-phase content of $\sim$90 wt% could be obtained.

Introduction

Silicon nitride has been acknowledged as one of the most promising materials (in many high-temperature structural applications, e.g., gas-turbine engines, cutting tools, bearings, and reciprocating engine parts) because of its high-temperature strength, thermal shock resistance, chemical stability, and excellent creep resistance [1, 2]. These properties partially originated from the transition from α to β phase at elevated temperatures ($\geq$1,400 °C), which results in the formation of needlelike structure. Si_3N_4 powders with high α-phase contents are, thus, usually used as the starting materials for these applications. Such powders (also with high specific surface areas) have also been shown to be suitable for application as catalyst supports for high temperature oxidation reactions of hydrocarbons [3]. Development of synthesis methods for the production of fine Si_3N_4 powders with high α-phase contents at low cost is thus an interesting research topic.

Among the various methods that have been developed for the synthesis of Si_3N_4, carbothermal reduction and nitridation has been utilized in industry as a major method for the production of Si_3N_4 powder [4–6]. In this method, SiO_2 and carbon powders are used as the precursor powders and they are first mixed and then react under a N_2 atmosphere in a furnace. The overall reaction can be expressed as:

$$3SiO_2 + 2N_2 + 6C \rightarrow Si_3N_4 + 6CO \quad (1)$$

and the reaction is believed to involve the following steps [7].

1. Reduction of SiO_2 and generation of SiO:

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)}, \quad (2)$$

$$SiO_{2(s)} + CO_{(g)} \rightarrow SiO_{(g)} + CO_{2(g)}. \quad (3)$$

2. Nitridation and heterogeneous nucleation of Si_3N_4:

$$3SiO_{(g)} + 2N_{2(g)} + 3C(s) \rightarrow Si_3N_{4(s)} + 3CO_{(g)}. \quad (4)$$

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3. Growth of Si_3N_4:

$$3SiO_{(g)} + 2N_{2(g)} + 3CO_{(g)} \rightarrow Si_3N_{4(s)} + 3CO_{2(g)}. \quad (5)$$

Among the reaction steps, conversion of SiO_2 to SiO (i.e., reactions 2 and 3) has been considered to dominate the formation rate of Si_3N_4, and the gas–solid reaction (i.e., reaction 3) is believed [8] to be slower than the solid–solid reaction (i.e., reaction 2). Since the solid–solid reaction can occur only at the contact points between the SiO_2 and carbon particles, the gas–solid reaction between CO and SiO_2 becomes the rate-limiting step for the formation of Si_3N_4 when the contact points between SiO_2 and carbon particles are consumed. Enhancement of the formation of Si_3N_4 by developing methods to increase the interfacial area between the precursor powders (i.e., SiO_2 and carbon) has thus been a research objective of many other studies. Zhang et al. [9] prepared ultrafine SiO_2 powders and mixed them with high specific surface area lamp black or activated carbon so as to increase the interfacial area between the precursor powders. They also mixed a SiO_2 powder with starch, which by thermal pyrolysis generated carbon with uniform distribution about the SiO_2 particles, thus, increasing the interfacial area between the precursor powders. Koc et al. [10] reported an improvement of contact area between the precursor powders by coating the SiO_2 particles with carbon, which was generated in situ by thermal pyrolysis of a hydrocarbon during coating. They also reported that due to an intimate contact between the precursor powders, Si_3N_4 with a more complete reaction, high α-phase content, and no agglomeration could be produced at a comparatively low temperature.

In the present study, a process was developed for the preparation of the precursor powders with a uniform mixing of nano-sized particles and a high-interfacial area by employing a solution combustion synthesis reaction. The development of the process will be described. The effects of important experimental parameters on the formation of Si_3N_4 and the α-phase content were investigated and will be presented and discussed.

Experimental

The synthesis process for Si_3N_4 powder was designed in the present study to consist of two stages. In the first stage, a homogeneous mixture of nano-sized SiO_2 and C powders (referred to as precursor powders hereafter) was produced by a solution combustion synthesis method. In the second stage, Si_3N_4 powder was produced from the precursor powders via a carbothermal reduction and nitridation method.

The characteristics of the reagents used in the present study are listed in Table 1. In the first stage of the synthesis process, either glycine or urea was used as the fuel, and ammonium nitrate was used as the oxidizer for the solution combustion reaction. In each of the experiments presented here, 4 g of the fuel (either glycine or urea) and stoichiometric amounts of the oxidizer were used according to the following reactions [11]:

Table 1 Characteristics of the reagents used in the present study

Reagent	Purity or concentration (wt%)	Melting or decomposition temperature (°C)	Manufacturer
Water glass	50	–	Rong Xiang Co.
NH_4NO_3	98	210	Nihon Shiyaku
Glycine	99	233	Sigma Aldrich
Urea	99	133	Showa
Sucrose	–	186	Showa

$$C_2O_2H_5N + 9/2NH_4NO_3 \rightarrow 2CO_2 + 23/2H_2O + 5N_2, \quad (6)$$

$$CO(NH_2)_2 + 3NH_4NO_3 \rightarrow CO_2 + 8H_2O + 4N_2. \quad (7)$$

An aqueous solution of 3.6 wt% silicic acid was used as the silicon source. The silicic acid was obtained from an aqueous solution of sodium silicate (water glass) by first diluting and then ion-exchanging for removing the sodium ions. The amounts of silicic acid used were expressed as the mass ratios of the silicic acid to the fuel and three ratios, i.e., 5:1, 3.3:1, and 2.5:1 were used in the present study. Since it was found that the residual carbon from the combustion of the fuel and the oxidizer was insufficient for the carbothermal reduction and nitridation reaction in the second stage, sucrose was added as an additional source of carbon. The amounts of sucrose used were expressed as the weight percentages of the amounts of silicic acid and three weight percentages, i.e., 0, 10, and 20 wt%, were used in the present study. In the experiments for the solution combustion synthesis of the precursor powders, fuel, oxidizer, and sucrose were added to the aqueous solution of silicic acid according to the desired quantities and ratios, and they were readily dissolved resulting in a homogeneous solution. The solution (contained in an alumina crucible) was first heated to 100 °C in a vacuum oven for the removal of water until a viscous mass was obtained. This viscous mass was then heated to 300 °C in a muffle furnace where the combustion reaction took place resulting in the formation of the precursor powders. In some of the experiments, the viscous mass was heated on a hot plate set at 300 °C for the combustion reaction to occur so that temperature measurement (by using a thermocouple) and observation of the combustion could be readily performed.

The precursor powders obtained from the solution combustion synthesis reaction were placed in a tube furnace (inside diameter: 69 mm) and heated under the flow of N_2 gas (1 L/min) for the carbothermal reduction and nitridation reaction. The product powders thus obtained were then heated in air at 600 °C for 4 h for the removal of residual carbon [8]. The final product (after the removal of residual carbon) was then analyzed for its crystalline phase, morphology, specific surface area, and oxygen content.

The crystalline phase was identified by X-ray diffraction (XRD, Rigaku, RINT2000, Japan) with CuKα radiation based on the standard of JCPDS. The morphology of the product was characterized by SEM (Joel, JSM-6700F, Japan) and TEM (Hitachi, H-7500, Japan). The specific surface area was obtained from N_2 adsorption according to the Brunauer–Emmett–Teller method (BET, Quantachrome, NOVA 1000e, USA). The oxygen content of the product was determined by using a nitrogen/oxygen analyzer (LECO, Joseph, MI, TC300, USA). The Si_3N_4 yield, defined as the percentage of the SiO_2 converted to Si_3N_4, was calculated based on the oxygen content measurement by assuming that the decrease in oxygen content was due to the conversion of SiO_2 to Si_3N_4. The temperature variation during the solution combustion synthesis reaction was measured by using 0.3-mm diameter K type thermocouples, which were insulated with 1.2-mm diameter alumina tubes. The temperature thus measured was recorded with a frequency of 50 data/s using a data acquisition system (Omega, DATAshuttle DS-16-8-TC, USA). The percentage of α-phase Si_3N_4 in the product was calculated using the following expression by applying the direct comparison method [12, 13]:

$$x_\alpha = 1/\left[1 + 0.668\left(I_\beta/I_\alpha\right)\right], \quad (8)$$

where I_α and I_β are the intensities of the XRD peaks of α and β phases corresponding to the crystal planes of (201) and (101), respectively, i.e., $2\theta = 31°$ for the (201) plane of α phase and $2\theta = 33°$ for the (101) plane of β phase.

Results

Solution combustion synthesis of precursor powders

Figures 1 and 2 show the temperature–time histories during the solution combustion synthesis reaction, when using urea or glycine as the fuel, respectively. In both Figs. 1 and 2, the weight ratios of silicic acid to fuel were kept at 5:1 and the amounts of sucrose added were 0, 10, and 20 wt% (with the corresponding temperature profiles (a), (b), and (c), respectively). In all the cases, evolution of smoke was observed when the viscous mass was heated to above 200 °C. When using urea as the fuel (Fig. 1), the combustion reaction was ignited at ~300 °C (taken as the point at which the temperature increases abruptly), and in the cases of using glycine (Fig. 2), the combustion reaction was ignited at a lower temperature, i.e., ~250 °C. In most of the cases (e.g., (b) and (c) in Fig. 1 and (a), (b), and (c) in Fig. 2), a flame (i.e., visible radiation) was observed during combustion but in other cases (e.g., (a) in Fig. 1), flameless or smoldering combustion was observed. Except in the case of smoldering combustion, the combustion causes a substantial increase in temperature and the

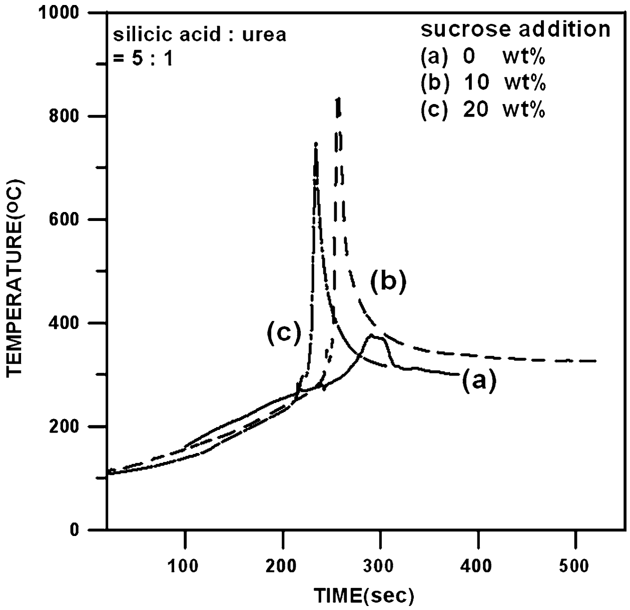

Fig. 1 Typical temperature–time histories during solution combustion synthesis reaction when using urea as the fuel

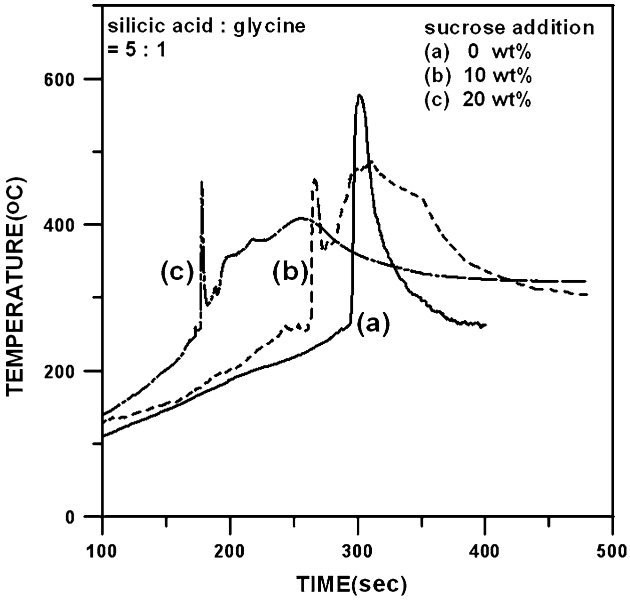

Fig. 2 Typical temperature–time histories during solution combustion synthesis reaction when using glycine as the fuel

maximum combustion temperature reaches 470–850 °C. In some cases (e.g., (a), (b), and (c) in Fig. 1 and (a) in Fig. 2), the combustion duration was relatively short (<50 s) but in other cases (e.g., (b) and (c) in Fig. 2), the combustion lasted for more than 100 s. In the latter cases, the combustion was observed to be composed of two stages: a flame-type combustion (creating the sharp peaks of the temperature profiles) in the first stage followed by a smouldering combustion (creating the broad peaks) in the second stage.

The solution combustion synthesis reaction resulted in the formation of the precursor powders, which were in a foam type and were black in color due to the presence of residual carbon (Fig. 3). As shown in Fig. 3, the precursor powders were observed to be composed of agglomerates (mostly 50–250 nm in size), which were made up of 10–20 nm primary particles. In order to quantify the residual carbon, the precursor powders were heated to 600 °C in air for 4 h. The precursor powders turned to white in color after the heating due to removal of the carbon by oxidation and the resulting white powders were SiO_2. The weight ratios of carbon to SiO_2 could thus be calculated for the precursor powders obtained from different compositions of the reactants and these are listed in Table 2. The specific surface areas of the SiO_2 powders were also measured and listed in Table 2. As indicated in Table 2, the precursor powders produced by using glycine contain greater amounts of carbon than those produced by using urea when comparing at the same percentages of sucrose addition. In addition, the SiO_2 powders produced by using glycine also possess larger specific surface areas than those produced by using urea. Consequently, glycine was used as fuel in most of the subsequent experiments presented in the present study.

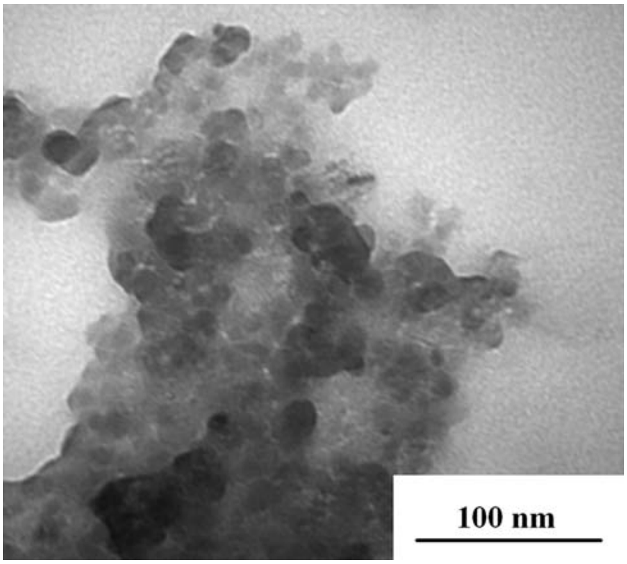

Fig. 3 A typical TEM photograph of the precursor powder prepared with silicic acid:glycine = 5:1 and 10 wt% sucrose addition

Table 2 Weight ratios of residual carbon to SiO_2 and the specific surface areas (SA) of SiO_2 in the precursor powders

Fuel	Weight ratio of silicic acid to fuel	Sucrose addition (wt%)	Weight ratio of residual carbon to SiO_2	SA of SiO_2 (m^2/g)
Glycine	5:1	0	1.2:1	340
Glycine	3.3:1	0	1.8:1	364
Glycine	2.5:1	0	2.4:1	409
Urea	5:1	0	0.5:1	305
Urea	5:1	10	2.0:1	188
Urea	5:1	20	3.6:1	243
Glycine	5:1	0	1.2:1	340
Glycine	5:1	10	2.8:1	538
Glycine	5:1	15	3.6:1	545
Glycine	5:1	20	4.4:1	552
Glycine	5:1	25	5.2:1	560

Carbothermal reduction and nitridation synthesis of Si_3N_4

In order to investigate the effect of the addition of sucrose, the carbothermal reduction and nitridation reaction was first performed using the precursor powders, which were synthesized with different ratios of silicic acid to glycine but with no addition (i.e., 0 wt%) of sucrose. The reaction temperature and time for the carbothermal reduction and nitridation reaction were 1,450 °C and 4 h, respectively. The XRD patterns of the products obtained from the precursor powders prepared with three different ratios (i.e., 5:1, 3.3:1, and 2.5:1) of silicic acid to glycine are shown in Fig. 4. As can be seen, no formation of Si_3N_4 could be detected as the ratio of silicic acid to glycine was 5:1 or 3.3:1 and the only compound detected in these two cases was SiO_2. As the silicic acid to glycine ratio was decreased to 2.5:1, formation of Si_3N_4 was apparent because strong peaks of Si_3N_4 were measured. In this case, the Si_3N_4 yield and the α-phase content were calculated to be 75 and 43 wt%, respectively. (All the yields and α-phase contents of the Si_3N_4 powders produced under various experimental conditions are listed in Table 3.) As indicated in Table 2 (and also marked in Fig. 4), the precursor powder prepared with the silicic acid to glycine ratio of 2.5:1 contains a higher carbon to SiO_2 ratio than those prepared with the silicic acid to glycine ratios of 3.3:1 and 5:1. A high carbon to SiO_2 ratio in the precursor powder was thus considered necessary for the formation of Si_3N_4. In the subsequent experiments presented in the present study, sucrose was thus added as an additional carbon source and a high ratio

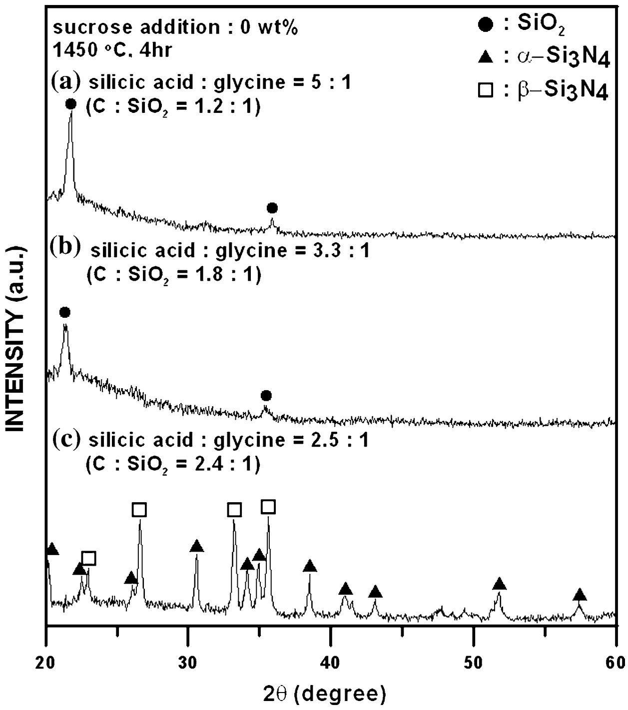

Fig. 4 XRD patterns of the as-synthesized products from carbothermal reduction and nitridation carried out at 1,450 °C for 4 h using the precursor powders prepared with three different silicic acid to glycine ratios (5:1, 3.3:1, and 2.5:1) but with no addition of sucrose

of silicic acid to glycine (i.e., 5:1) was used because a larger amount of the desired product (Si_3N_4) could be produced with a higher silicic acid to glycine ratio.

The XRD patterns of the products obtained from the precursor powders, which were prepared with a silicic acid to glycine ratio of 5:1 but with different percentages of sucrose addition, i.e., 0, 10, 15, 20, and 25 wt%, respectively, are shown in Fig. 5. As mentioned previously, no formation of Si_3N_4 was detected (Fig. 5a) when no sucrose was added. With additions of 10 and 15 wt% of sucrose, Si_3N_4 is seen to be formed and the yields and α-phase contents were calculated to be 78 and 45 wt%, respectively, for 10 wt% sucrose addition (Fig. 5b) and both 68 wt% for 15 wt% sucrose addition (Fig. 5c). When the sucrose addition was increased to 20 wt% or higher, formation of Si_3N_4 was seen to be suppressed (yield = 40 and 15 wt% for 20 and 25 wt% sucrose addition, respectively.); and in the mean time, SiC was detected to be formed (Fig. 5d, e). Based on the results shown in Fig. 5, it was considered that 10 wt% of sucrose addition was appropriate for the formation of Si_3N_4. This percentage of sucrose addition was thus used in the subsequent experiments aimed at studying the temperature effect.

The XRD patterns of the products from the carbothermal reduction and nitridation reaction carried out at three different temperatures, i.e., 1,400, 1,425, and 1,450 °C, but with the same reaction time (4 h) are shown in Fig. 6. The precursor powders used were all prepared with a silicic acid to glycine ratio of 5:1 and a sucrose addition of 10 wt%. As can be seen, Si_3N_4 could be produced at all the three temperatures but with higher yields at 1,425 and 1,450 °C (yield = 77 and 78 wt%, respectively) than that at 1,400 °C (yield = 30 wt%). The α-phase content was calculated to be 88 wt% in the case of 1,425 °C, which is higher than in the other cases, i.e., 70 wt% at 1,400 °C and 45 wt% at 1,450 °C.

In order to study the effect of reaction time, the carbothermal reduction and nitridation reaction was carried out at 1,425 °C for five different time durations, i.e., 2, 3, 4, 5,

Table 3 The yields and α-phase contents of the Si_3N_4 powders produced under various experimental conditions

Sample	Fuel	Weight ratio of silicic acid to fuel	Sucrose addition (wt%)	Weight ratio of residual carbon to SiO_2	Temperature (°C)	Time (h)	Yield (wt%)	α-Phase content (wt%)
Fig. 5c	Glycine	2:5:1	0	2:4:1	1,450	4	75	43
Fig. 6b	Glycine	5:0:1	10	2:8:1	1,450	4	78	45
Fig. 6c	Glycine	5:0:1	15	3:6:1	1,450	4	68	68
Fig. 7a	Glycine	5:0:1	10	2:8:1	1,400	4	30	70
Fig. 7b	Glycine	5:0:1	10	2:8:1	1,425	4	77	88
Fig. 7c	Glycine	5:0:1	10	2:8:1	1,450	4	78	45
Fig. 8a	Glycine	5:0:1	10	2:8:1	1,425	2	7	–
Fig. 8b	Glycine	5:0:1	10	2:8:1	1,425	3	13	–
Fig. 8c	Glycine	5:0:1	10	2:8:1	1,425	4	77	88
Fig. 8d	Glycine	5:0:1	10	2:8:1	1,425	5	78	86
Fig. 8e	Glycine	5:0:1	10	2:8:1	1,425	6	82	85
Fig. 9b	Urea	5:0:1	20	3:6:1	1,425	4	64	96
Fig. 9c	Glycine	5:0:1	10	2:8:1	1,425	4	77	98

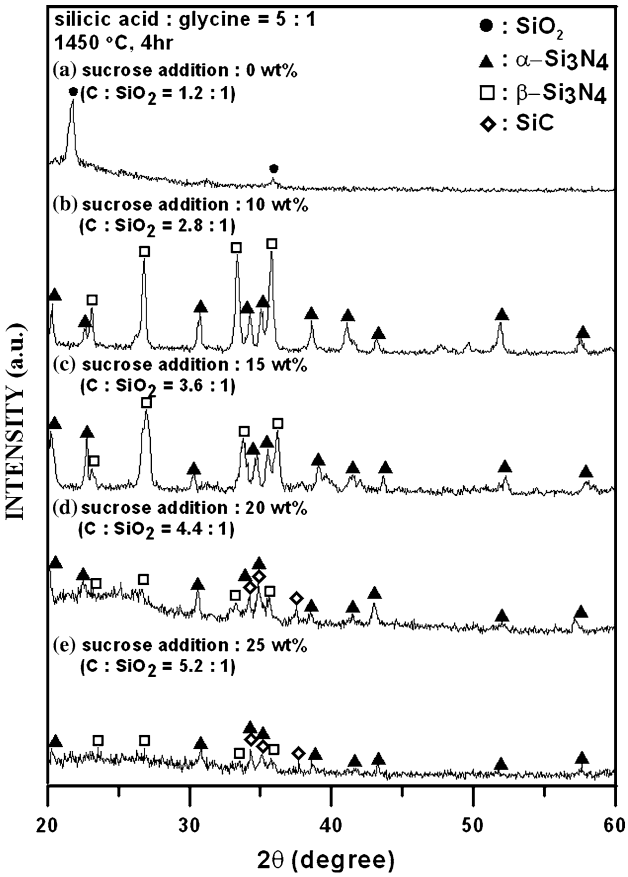

Fig. 5 XRD patterns of the as-synthesized products from carbothermal reduction and nitridation carried out at 1,450 °C for 4 h using the precursor powders prepared with silicic acid:glycine = 5:1 and with 0, 10,15,20, and 25 wt% sucrose addition

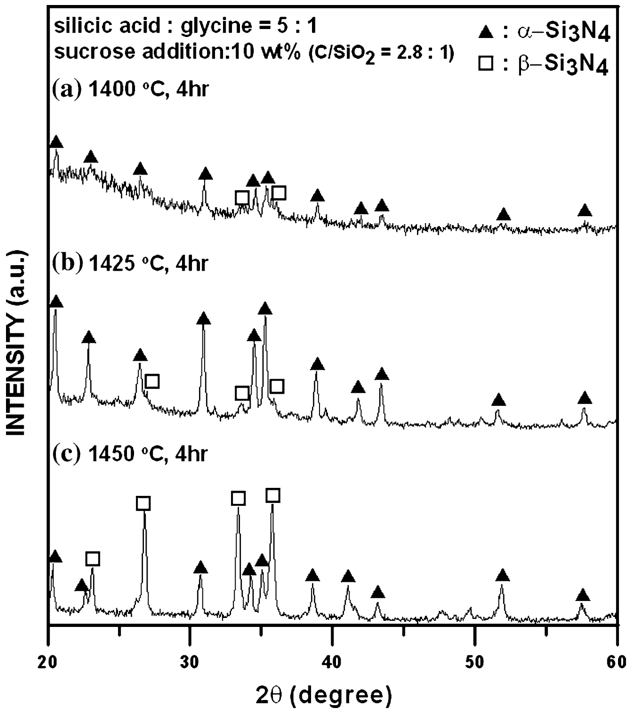

Fig. 6 XRD patterns of the as-synthesized products from carbothermal reduction and nitridation carried out at three different temperatures (1,400, 1,425, and 1,450 °C) for 4 h using the precursor powders prepared with silicic acid:glycine = 5:1 and 10 wt% sucrose addition

and 6 h; and the XRD patterns of the products are shown in Fig. 7a–e, respectively. The precursor powders were all prepared with a silicic acid to glycine ratio of 5:1 and a sucrose addition of 10 wt%. As can be seen, although Si_3N_4 could be produced with all the reaction time durations, the yields with 2 and 3 h are relatively low (yield = 7 and 13 wt%, respectively). A much higher yield was obtained when the reaction time was increased to 4, 5, and 6 h and the yields were calculated to be 77, 78, and 82 wt%, respectively. In these cases, the α-phase contents of the products were calculated to be 88, 86, and 85 wt% for the reaction times of 4, 5 and 6 h, respectively.

Although glycine was selected as the fuel for the above systematic study, urea was also tested for the synthesis of Si_3N_4. Figure 8a, b are the XRD patterns of the products synthesized when using the precursor powders prepared with urea as the fuel. In both cases, the silicic acid to urea ratios were kept at 5:1 and the carbothermal reduction and nitridation reactions were carried out at 1,425 °C for 4 h. As can be seen, no formation of Si_3N_4 could be detected when using the precursor powder prepared with 10 wt% sucrose addition (Fig. 8a). However, Si_3N_4 with a yield of 64 wt% was obtained when 20 wt% of sucrose was added in the preparation of the precursor powder (Fig. 8b), and in this case, the α-phase content of the product was calculated to be 96 wt%. For comparison, the XRD pattern of the product synthesized under similar conditions but with glycine as the fuel was shown as Fig. 8c and that of a commercially available Si_3N_4 (manufactured by Alfa Aesar with a reported α-phase content of 85 wt%) was also shown as Fig. 8d. By comparison, the Si_3N_4 powders synthesized in the present study (Fig. 8b, c) seem to contain higher contents of α phase than the commercial product.

A typical SEM photograph of the Si_3N_4 powder obtained from the carbothermal reduction and nitridation synthesized product by first removing the residual carbon and then removing the residual SiO_2 by washing it with a hydrofluoric acid is shown in Fig. 9. As can be seen, the powder is mostly composed of agglomerated particles with 0.1–0.2 μm in diameter. The powder also contains a minor amount of rod-shape crystals with a diameter of 0.2 μm and a length of up to tens of micrometers, which are thought to be the β-phase Si_3N_4. The specific surface area of the powder was measured to be 7.2 m^2/g.

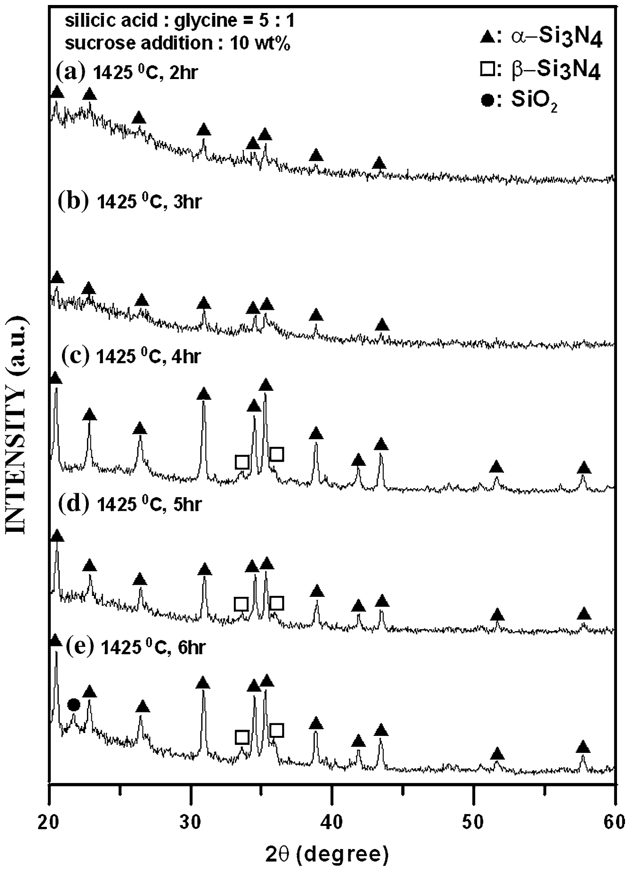

Fig. 7 XRD patterns of the as-synthesized products from carbothermal reduction and nitridation carried out at 1,425 °C for different time durations (2, 3, 4, 5, and 6 h) using precursor powders prepared with silicic acid:glycine = 5:1 and 10 wt% sucrose addition

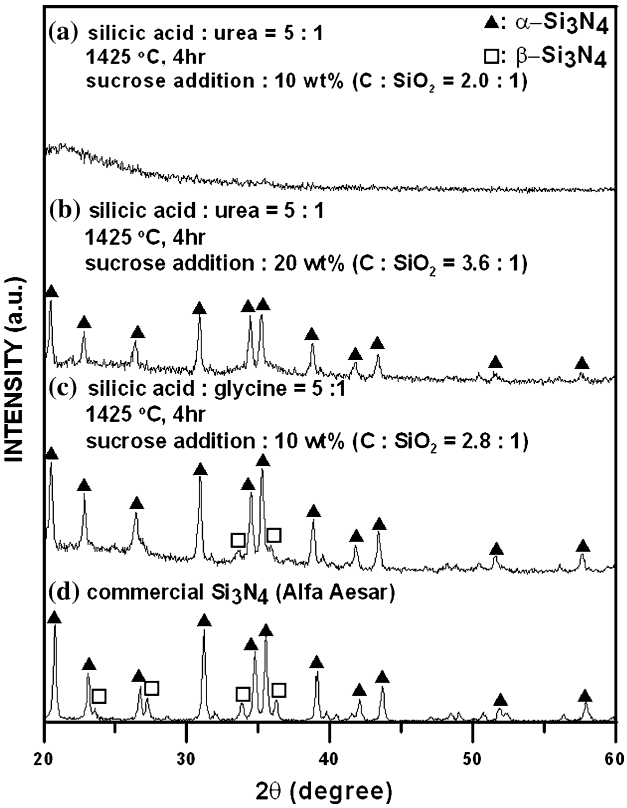

Fig. 8 XRD patterns of the as-synthesized products obtained by using precursor powders prepared under different conditions: **a** using urea as fuel with 10 wt% sucrose addition; **b** using urea as fuel with 20 wt% sucrose addition; and **c** using glycine as fuel with 10 wt% sucrose addition; and **d** XRD pattern of a Si_3N_4 powder manufactured by Alfa Aesar

Discussion

As mentioned previously, among the reaction steps involved in the carbothermal reduction and nitridation synthesis of Si_3N_4, conversion of SiO_2 to SiO has been considered to dominate the formation rate of Si_3N_4 [8–10]. At the initial stage, SiO_2 and carbon particles, which are in contact, can react to generate SiO and CO (i.e., reaction 2). Once CO is formed, conversion of SiO_2 to SiO can occur via the reaction of CO and SiO_2 (i.e., reaction 3). However, this gas–solid reaction is considered [8] to be slower than the solid–solid reaction (i.e., reaction 2). Since the solid–solid reaction can occur only at the contact points between SiO_2 and carbon particles, the gas–solid reaction becomes the rate-limiting step when the contact points between SiO_2 and carbon particles are consumed. One way to promote the formation of Si_3N_4 is thus to increase the interfacial area (or contact points) between SiO_2 and carbon particles. This can be effectively achieved by using SiO_2 and carbon

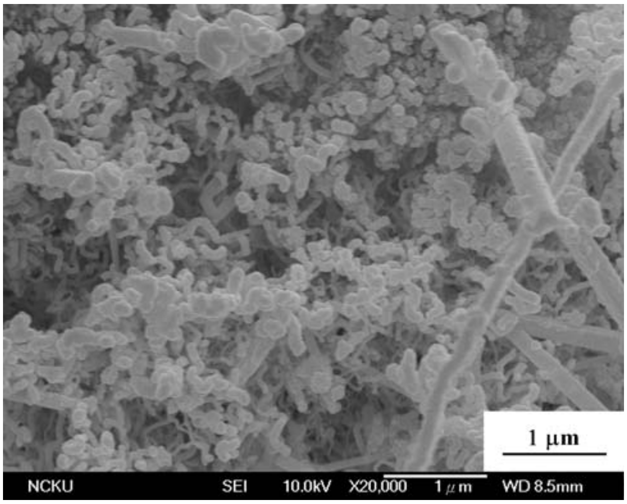

Fig. 9 A typical SEM photograph of the Si_3N_4 powder after removal of residual C and SiO_2. The carbothermal reduction and nitridation was carried out at 1,425 °C for 4 h using the precursor powder prepared with silicic acid:glycine = 5:1 and 10 wt% sucrose addition

particles with fine particle size and by improving the mixing between them [10].

In the present study, the contact between SiO_2 and carbon particles was improved by preparing the precursor powders via a solution combustion synthesis reaction. The solution combustion synthesis reaction is a kind of method for the synthesis of fine particles by utilizing exothermic and self-sustaining reactions (i.e., the combustion reactions) of reactants, which are initially dissolved in water as a homogeneous solution [14, 15]. In the present study, the fuel and the oxidizer are the primary reactants for the combustion reaction. This combustion reaction creates a high temperature environment causing a rapid generation of SiO_2-forming species from oxidation of silicic acid and a rapid generation of carbon from pyrolysis of sucrose (and partially from the fuel). Nano-sized particles with uniform distribution can be readily produced because of the following characteristics of the solution combustion synthesis reaction. (1) The reactants are mixed on a molecular scale because they are all dissolved completely in a solution. (2) The time duration for the reaction and particle formation is relatively short (less than 1 or 2 min as can be seen by the temperature profiles shown in Figs. 1 and 2), little compositional segregation can occur and the time available for particle growth is limited. (3) The maximum combustion temperature is low (usually <1000 °C, and usually well below the melting points of the product materials), little agglomeration and coalescence of the particles can occur. (4) A large amount of gas is generated and released during reaction, which further prevents the particles from agglomeration and coalescence.

The precursor powders prepared in the present study were thus homogeneous mixtures of nano-sized SiO_2 and carbon particles as a result of the solution combustion synthesis reaction. (The nano-sized characteristics were seen by the TEM photograph in Fig. 3 and by the high specific surface areas of the SiO_2 particles as listed in Table 2.) As expected, Si_3N_4 could be synthesized with carbon generated from different sources, i.e., from fuel only (Fig. 4c) or from a combination of fuel and sucrose (e.g., Figs. 5b, 8b). However, based on the results shown in Figs. 4, 5, and 8, it is seen that the yield of Si_3N_4 is strongly affected by the carbon to SiO_2 ratio (in the precursor powder). These data were analyzed by plotting the yield versus the C/SiO_2 ratio. As can be seen in Fig. 10, formation of Si_3N_4 can be detected only when C/SiO_2 is greater than ~2.0 and the Si_3N_4 yield increases rapidly with increasing C/SiO_2 to a maximum at $C/SiO_2 = \sim 2.8$, and then begins to decrease with further increase in C/SiO_2. The enhancement of yield by increasing C/SiO_2 ratio has also been found in many other studies [9, 16]. This can be explained by the fact that high C/SiO_2 ratios promote the formation of SiO (i.e., reactions 2 and 3) and that excess carbon provides more nucleation sites for the Si_3N_4 formation (i.e., reaction 4). However, it was not mentioned in these studies that the formation of Si_3N_4 is suppressed at high C/SiO_2 ratios (e.g., $C/SiO_2 = 4.4:1$ as found in the present study). For example, Komeya and Inoue [16] studied the carbothermal reduction and nitridation synthesis of Si_3N_4 by preparing precursor powders by mixing silica and carbon powders. They found that the Si_3N_4 yield increases rapidly with increasing C/SiO_2 molar ratio up to 20 (equivalent to a weight ratio of 4:1) and then increases slowly up to 60 (equivalent to a weight ratio of 12:1), the maximum C/SiO_2 molar ratio reported by them. The suppression of Si_3N_4 formation found in the present study may be explained by retardation on the diffusion of nitrogen by great amounts of carbon surrounding the silica particles.

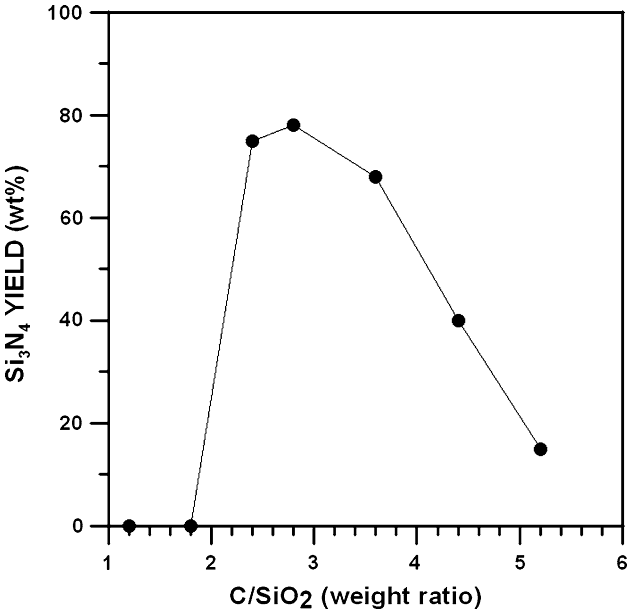

Fig. 10 Effect of C/SiO_2 weight ratio on Si_3N_4 yield

Many previous studies [7, 8] pointed out that high C/SiO_2 ratios favor the formation of α phase because the α-phase formation is associated with C and its related species Si–O–C. Many other studies [10, 16] also pointed out that high reaction temperatures favor the formation of β phase. Similar phenomena were also found in the present study. As can be seen in Fig. 8, the α-phase content increases from 88 wt% (Fig. 8c) to 96 wt% (Fig. 8b) as the C/SiO_2 ratio is increased from 2.8 to 3.6, and in Fig. 6, the β phase content increases significantly (from 12 to 55 wt%) as the temperature is increased from 1,425 to 1,450 °C.

It is well known that SiC will be formed at high-reaction temperatures and many other studies [9, 16] pointed out that the critical temperature for the SiC formation is above 1,450–1500 °C. In the present study, it was found that SiC formation is related to the C/SiO_2 ratio. As can be seen in

Figs. 4 and 5 where the temperatures were both kept at 1,450 °C, SiC was not detected at $C/SiO_2 = 2.4$, 2.8, and 3.6 (Figs. 4c, 5b, c), but was detected at $C/SiO_2 = 4.4$ and 5.2 (Figs. 5d, e).

Conclusion

Silicon nitride with high α-phase contents was successfully synthesized via carbothermal reduction and nitridation process by using precursor powders prepared by a solution combustion synthesis method. The solution combustion synthesis method produces homogeneous mixtures of nano-sized carbon and SiO_2 particles and the carbon to SiO_2 ratio can be readily controlled by adjusting the reactant composition. When the carbothermal reduction and nitridation reaction was carried out at 1,425–1,450 °C for 4 h, formation of Si_3N_4 can be detected only when the C/SiO_2 weight ratio is greater than ~2.0. The Si_3N_4 yield increases rapidly as the C/SiO_2 weight ratio is increased from ~2.0 to 2.8 and decreases with further increase in the C/SiO_2 ratio. SiC was detected to be formed at 1,450 °C only when the C/SiO_2 weight ratio was increased to 4.4 and higher. The α-phase content increases with increasing C/SiO_2 weight ratio and decreases with increasing temperature. Depending on the C/SiO_2 ratio, a Si_3N_4 yield of ~80 wt% and an α-phase content of ~90 wt% could be obtained.

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References

1. Riley FL (2000) J Am Ceram Soc 832:45
2. Lis J, Majorowski S, Hlavacek JA (1991) Ceram Bull 70:244
3. Methivier C, Massardier J, Bertolini JC (1999) Appl Catal A Gen 182:337
4. Guo C, Xing Z, Ma X, Xu L, Qian Y (2008) J Am Ceram Soc 91:1725
5. Wu XC, Song WH, Zhao B, Huang WD, Pu MH, Sun YP, Du JJ (2000) Solid State Commun 115:683
6. Yang JF, Shan SY, Janssen R, Schneider G, Ohji T, Kanzaki S (2005) Acta Mater 53:2981
7. Vlasova MV, Bartnitskaya TS, Sukhikh LL, Krushinskaya LA, Tomila TV, Artyuch SY (1997) J Mater Sci 30:5263. doi: 10.1007/BF00356080
8. Weimer AW, Eisman GA, Susnitzky DW, Beaman DR, McCoy JW (1997) J Am Ceram Soc 80:2853
9. Zhang SC, Cannon WR (1984) J Am Ceram Soc 67:691
10. Koc R, Kaza S (1998) J Eur Ceram Soc 18:1471
11. Lima MD, Bonadimann R, de Andrade MJ, Toniolo JC, Bergmann CP (2006) J Eur Ceram Soc 26:1213
12. Cullite BD (1978) Elements of X-ray diffraction. Addison-Wesley, London
13. Real C, Alcala MD, Criad JM (2004) J Am Ceram Soc 87:75
14. Patila KC, Arunab ST, Mimania T (2002) Curr Opin Solid State Mater Sci 6:507
15. Kuang J, Zhang C, Zhou X, Wang S (2003) J Cryst Growth 256:288
16. Komeya K, Inoue H (1975) J Mater Sci Lett 10:1243