Synthesis of β-Si₃N₄ powder from quartz via carbothermal reduction nitridation

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Abstract

β-Si₃N₄ powder was synthesized via carbothermal reduction nitridation (CRN) method using quartz as starting material. The influence of synthesis temperature, C/SiO₂ molar ratio and amount of Fe₂O₃ additive on the phase transformation and micro-morphology of β-Si₃N₄ powder was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The results showed that the optimal experimental conditions for the CRN synthesis of β-Si₃N₄ powder were 3 h sintering at 1600 °C in flowing nitrogen atmosphere with C/SiO₂ molar ratio of 2.0 and amount of Fe₂O₃ additive of 5.0 wt.%. The prepared β-Si₃N₄ grains present a short hexagonal, rod-like morphology. Changes in experimental parameters affect the phase compositions and the morphology of the product. Excessive carbon promoted the formation reaction of β-SiC. Fe₂O₃ additive exerted a significant promotion on the formation of β-Si₃N₄ in CRN process by forming the low melting point eutectics.

Keywords:
β-Si₃N₄ powder
Controllable synthesis
Quartz
Carbothermal reduction nitridation

1. Introduction

Silicon nitride (Si₃N₄) based materials, as one of the most important advanced structural ceramics, exhibit excellent mechanical properties, and good oxidation resistance, thermal and chemical stability both at room and high temperatures [1,2]. Due to these desirable properties, Si₃N₄ has been extensively studied and has become the most promising structural material especially for high temperature applications [3,4].

It is known that α-Si₃N₄ starting powders have a higher reactivity and are used more widely than β-Si₃N₄ powder [1,4]. It is generally accepted that α-Si₃N₄ powder is the preferred raw material for fabricating compacted bodies because the α-Si₃N₄ starting powder is an easy attainment of elongated Si₃N₄/SiAlON grain morphology which has excellent mechanical properties [5–7]. On the other hand, when β-Si₃N₄ powder is used as starting powder, the formation and densification of the elongated β-Si₃N₄ grain are rather difficult. However, the high cost of fine α-Si₃N₄ powder is the major obstacles for large scale applications of Si₃N₄ based materials. Recently, it was reported that the high-cost problem can be overcome by using fine-grained (<0.5 μm) β-Si₃N₄ powder as the starting powder and applying appropriate post-sintering heat treatment schedules [8–10]. Hence, it is possible to achieve good mechanical properties with β-Si₃N₄ as the starting powder by means of that method. For this reason, it is significant to develop a low-cost synthesis technique for high quality β-Si₃N₄ powder.

To date, several methods have been employed to produce Si₃N₄ powder from various silicon sources, such as direct nitridation of silicon powder, carbothermal reduction nitridation (CRN) of silica, gas-phase reaction of silane, thermal decomposition of silicon diimide, etc. The CRN method has been the most promising candidate for low-cost synthesizing Si₃N₄ materials from natural minerals [11-14]. In previous works, many researches focused on the CRN of various raw materials, which are aiming at extending the knowledge about the reaction kinetics, thermodynamics and mechanism of the CRN process. It was reported that the physical and chemical state of the starting materials, i.e., the homogeneity of mixtures, and the specific surface area, exerted a significant influence on producing the Si₃N₄ by CRN method [6,11,15]. Durham et al. [15] and Ekeland et al. [16] revealed that the particle size of starting materials affected the amount of α-Si₃N₄. Cho and Charles [17] reported that the amount of α-Si₃N₄ formed and the percent weight loss of the reaction products increased with a decreasing carbon particle size, the reaction rate can be increased dramatically when a finer silica powder is used in the starting mixture. Kurt and Davies [18] also showed that changes in process parameters such as temperature and heating rate affected the particle morphology and size of the formed powders. Weimer et al. [19] studied the effect of “seed” α-Si₃N₄ in the CRN process of α-Si₃N₄, and found that the synthesis reactions followed a nucleation-growth mechanism. It was also reported that fine-grained α-Si₃N₄ powder was produced from colloidal SiO₂, which contained premixed sintering additives of oxides such as MgO and Y₂O₃ [20].

Furthermore, lots of outstanding works have also been performed to investigate the influence of the experimental conditions on the rate of formation of Si₃N₄ in a CRN process. Studies by Kurt and Davies [21] revealed that the liquid phases of oxides such as Al₂O₃, K₂O, CaO, TiO₂ and Fe₂O₃ promote the formation of β-Si₃N₄ instead of the preferred α-Si₃N₄. Arik et al. [22,23] demonstrated that the formation of β-Si₃N₄ instead of α-Si₃N₄ was controlled by the oxides. The results of Liou and Chang [24] showed that the particle size of the raw materials is
an important parameter for the formation rate of Si₃N₄. Besides, the formation rate of α-Si₃N₄ in CRN process was reported to be dependent on the specific surface area of the carbon [15], but in contrast, the specific surface area or the particle size of SiO₂ had no significant effect on the extent of conversion [6,11,14,15]. However, the main problems of these reported studies for the Si₃N₄ synthesis via CRN method include a high SiC amount and residual carbon existing in the products. Besides, to the best of our knowledge, no work on the synthesis of β-Si₃N₄ powder from natural quartz has been reported in the literature. Therefore, it is valuable and important to investigate the suitable experimental conditions for controllable synthesis of low cost β-Si₃N₄ powder.

In this study, quartz and carbon coke powders were selected as raw materials to prepare β-Si₃N₄ powder via CRN method. The influence of synthesis temperature, C/SiO₂ molar ratio and amount of Fe₂O₃ additive on the phase transformation and micro-morphology of β-Si₃N₄ powder was studied. Moreover, the in-situ synthesis mechanism of β-Si₃N₄ powder was analyzed. This paper concentrated on the cost-effective synthesis of β-Si₃N₄ powder. This study would provide a feasible approach and a new perspective for the comprehensive application of β-Si₃N₄ in various fields, specifically, Si₃N₄ based structural ceramics, advanced refractories and wear resistant materials.

2. Materials and methods

2.1. Material preparation

The main starting materials employed in this study were as follows: natural quartz powder (granularity ≤38 μm, chemical composition (wt.%): SiO₂: 97.8, Al₂O₃: 0.63, Fe₂O₃: 0.13, CaO: 0.08, K₂O: 0.05, others: 1.03), carbon coke powder (granularity≤74 μm, carbon content=88 wt.%, Shanxi Xinxihai Imp. & Exp. Co., Ltd., China), Fe₂O₃ (A.R. grade, Sinopharm Chemical Reagent Beijing Co., Ltd., China) was used as the sintering additive. The starting material powders were mixed according to Table 1. The mixtures were prepared by mixing the starting material powders and the sintering additive with various C/SiO₂ molar ratios and different Fe₂O₃ addition, respectively. As starting powders were weighed, agate balls were used as the milling media and mixed with the powder mixture at a ball-to-powder weight ratio of 5:1. The starting materials and agate balls were put into the polyurethane jar and starting powders were milled for 6 h in anhydrous alcohol. Then the oven dry powders (dried at 70 °C for 12 h) were placed in a graphite crucible and the whole set-up was placed in the center of a tube furnace. The furnace temperature was initially raised to 1000 °C at a heating rate of 10 °C/min, then heating continued at 5 °C/min to the final temperature which was maintained for a further 3 h. The CRN reactions were carried out at different final temperatures (1500 °C, 1520 °C, 1540 °C, 1560 °C, 1580 °C and 1600 °C) for 3 h in a high purity flowing nitrogen gas (purity 99.99%) with a pressure of 0.2 MPa. Then the samples were slowly cooled down (200 °C·h⁻¹) to room temperature. After the CRN process, the products were heated in air for 1 h at 700 °C for residual carbon burning.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>C/SiO₂ molar ratio</th>
<th>Batch composition</th>
<th>Addition Fe₂O₃</th>
<th>Fe₂O₃—C→FeO(l) + CO(g)</th>
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<tbody>
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<td>S1</td>
<td>2.0</td>
<td>73.04</td>
<td>32.46</td>
<td>2.5</td>
</tr>
<tr>
<td>S2</td>
<td>2.2</td>
<td>73.04</td>
<td>34.09</td>
<td>2.5</td>
</tr>
<tr>
<td>S3</td>
<td>2.4</td>
<td>73.04</td>
<td>35.71</td>
<td>2.5</td>
</tr>
<tr>
<td>S4</td>
<td>3.0</td>
<td>73.04</td>
<td>38.95</td>
<td>2.5</td>
</tr>
<tr>
<td>T1</td>
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<td>32.46</td>
<td>0</td>
</tr>
<tr>
<td>T2</td>
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<td>73.04</td>
<td>32.46</td>
<td>5.0</td>
</tr>
</tbody>
</table>

2.2. Characterization

The crystalline phases as well as the amounts of the synthesized products were determined by X-ray diffraction (XRD; D8 Advance diffractometer, Germany), using Cu Kα₁ radiation (λ = 1.5406 Å) with a step of 0.02° (2θ) and a scanning rate of 4°·min⁻¹. Integrated peak areas were used to determine the relative amounts, using standard procedures [25]. The micro-morphologies and micro-area chemical analysis of the products were examined by scanning electron microscopy (SEM: JEM-6460LV microscope, Japan), energy dispersive spectroscopy (EDS, INCA X-sight, Oxford Instrument, UK), transmission electron microscopy (TEM, JEM-L1000, Japan, accelerating voltage 200 keV, 4 k × 2.7 k Gatan CCD camera), and high-resolution transmission electron microscopy (HRTEM, JEM2010, Japan). Powders for TEM observation were dispersed in absolute ethanol by ultrasonication (KQ-100DB) for 30 min, and a drop of the suspension containing the products was dropped onto a copper grid coated with an amorphous carbon supporting film and then dried in air.

3. Results and discussion

3.1. Influence of the amount of Fe₂O₃ additive on phase composition of products

In order to study the influence of the amount of Fe₂O₃ additive on phase composition of products, we compared the XRD patterns of the products with the addition of various amounts of Fe₂O₃ additive. Fig. 1(a) shows the XRD pattern of samples T1, S1 and T2 sintered at 1580 °C for 3 h. It can be observed that β-Si₃N₄ and β-SiC were the main crystalline phases in the products of samples T1, S1 and T2. With the increase of the additive amount, the diffraction peaks deriving from β-Si₃N₄ became stronger gradually. Precise XRD patterns from 22° to 35° of samples T1, S1 and T2 are given in Fig. 1(b). It reveals that the X-ray intensities of (110), (200) and (101) diffraction peaks of β-Si₃N₄ were enhanced significantly. Fig. 1(c) shows the plot of β-SiC and β-Si₃N₄ amount versus the amount of Fe₂O₃ additive. It is shown clearly that, with the amount of Fe₂O₃ additive, the amount of β-Si₃N₄ increased from 24.1% to 40.2%, while that of β-SiC dropped from 75.9% to 55.0%. Therefore, the formation process of β-Si₃N₄ could be promoted by increasing the amount of Fe₂O₃ additive.

Under normal conditions, CRN method produces a very high α-Si₃N₄ content (>95% phase purity) powder. However, in the presence of metallic impurities, such as K₂O, Na₂O, TiO₂, Al₂O₃, Fe₂O₃ and CaO contained in the starting materials, β-Si₃N₄ formation is associated with the existence of low-melting eutectics [15,18,21,22]. Therefore, the Fe₂O₃ additive and impurities existing in the starting powders are the important reason for high β-Si₃N₄ content in the product during our study.

A small diffraction peak was detected around 2θ = 45.4° suggesting the presence of Fe-Si. As reported in the literature by Kurt and Davies [18,21], impurity oxides like Al₂O₃, K₂O, TiO₂, Fe₂O₃ and CaO would result in the formation of low melting point eutectics such as Fe-Si with SiO₂. During the CRN procedure, Fe-Si was generated by the reactions of Fe₂O₃, SiO₂ and C according to the following reactions:

$$\text{Fe}_2\text{O}_3(s) + C(s) \rightarrow \text{FeO}(l) + \text{CO}(g)$$

(1)

$$\text{FeO}(l) + \text{SiO}_2(l) + C(s) \rightarrow \text{Fe}_2\text{Si}(l) + \text{CO}(g)$$

(2)

As the formation of the liquid phase, the deposition of intermediate silicon monoxide (SiO) occurred in the liquid phase. β-Si₃N₄ seed originated from the supersaturation of the liquid grew gradually to form fine equiaxed columnar β-Si₃N₄ grain by precipitation from the liquid at the liquid–solid interface. During this deposition–nucleation–precipitation process, vapor–liquid–solid (VLS) reactions occurred.
with those liquid phases acting as the nucleation sites. It is therefore deduced that, in the CRN process, the formation of the liquid phase eutectics promoted the nucleation process of $\beta$-Si$_3$N$_4$ by increasing the nucleation sites remarkably. Furthermore, the addition of Fe$_2$O$_3$ additive also had an important effect on the CRN process for the synthesis of $\beta$-Si$_3$N$_4$ powder by lowering the reaction time and the sintering temperature[20]. Therefore, Fe$_2$O$_3$ additive exerted a significant promotion on the formation of $\beta$-Si$_3$N$_4$ in CRN process by forming the low melting point eutectics. In our study, 5.0 wt.% addition of Fe$_2$O$_3$ additive was more suitable for the formation of $\beta$-Si$_3$N$_4$ using quartz as the starting material via CRN process.

3.2. Influence of the temperature on phase composition and micro-morphology of products

The crystalline phase evolution of quartz fired at different reaction temperatures was further investigated. The XRD patterns of the sample S1 sintered at different temperatures (1500 °C, 1540 °C, 1580 °C and 1600 °C) for 3 h are shown in Fig. 2. It can be seen that the reaction products were a mixture of cristobalite and residual quartz at 1500 °C, but small quantities of $\beta$-SiC and Si$_2$N$_2$O appeared in the products. It is generally accepted that the CRN reaction of quartz occurred through step by step mechanism, and SiO acted as a gaseous intermediate [6,7,19]. The gaseous SiO was produced by the reaction of SiO$_2$ with carbon according to the reactions (3) and (4). Subsequently, SiO reacted with carbon and produced Si$_2$N$_2$O and $\beta$-SiC in accordance with reaction (5) and reaction (6), respectively. It is believed that the physical contact between carbon particles and silicon dioxide particles was essential for the SiO formation [5,7,26]. So the CRN process was sensitive to the physical state of carbon incorporated in quartz. The XRD results also indicate that the nitridation reaction of quartz was incomplete. As mentioned above, the small peak around 45.4° was due to the presence of the Fe$_3$Si. Furthermore, a broad hump was detected around 2θ = 20–30° might imply the presence of
an amorphous phase at 1500 °C. At temperatures above 1500 °C, an increasing number of Si2N2O and β-SiC were observable. At 1540 °C, the residual quartz and cristobalite almost disappeared, while β-SiC became apparent.

SiO2(s) + C(s) → CO(g) + SiO(g)  \hspace{1cm} (3)

SiO2(s) + CO(g) → CO2(g) + SiO(g)  \hspace{1cm} (4)

SiO(g) + 2C(s) → SiC(s) + CO(g)  \hspace{1cm} (5)

2SiO(g) + N2(g) + C(s) → Si3N4(s) + 2CO(g)  \hspace{1cm} (6)

When the temperature increased to 1580 °C, the amount of Si2N2O and β-SiC increased, but that of the cristobalite and residual quartz disappeared. Besides, β-Si3N4 appeared in the products and became the predominant crystalline phase when the synthesis temperature was above 1580 °C (Fig. 2). This was the result of the carbonitriding reactions (7) and (8). At 1600 °C, the diffraction peak intensity of β-Si3N4 was higher than that obtained at 1580 °C while the diffraction peaks of β-SiC phase were barely discernible. It is inferred that Si2N2O reacted according to the carbonitriding reaction (9) to form β-Si3N4. Therefore, the temperature of 1600 °C and the duration of 3 h were favorable for the CRN synthesis of β-Si3N4 powder from quartz in 0.2 MPa flowing nitrogen atmosphere.

3SiO(g) + 2N2(g) + 3C(s) → Si3N4(s) + 3CO(g)  \hspace{1cm} (7)

3SiO2(s) + 2N2(g) + 6C(s) → Si3N4(s) + 6CO(g)  \hspace{1cm} (8)

3Si3N2O(s) + N2(g) + 3C(s) → 2Si3N4(s) + 3CO(g)  \hspace{1cm} (9)

SiO(g) + 3CO(g) → SiC(s) + 2CO2(g)  \hspace{1cm} (10)

For investigating the micro-morphologies of the products, we compared SEM images and EDS spectrums of the products, respectively.

Fig. 3. SEM micrographs of sample S1 sintered at different temperatures for 3 h: (a) 1500 °C; (b) 1540 °C; (c) 1580 °C; (d) 1600 °C; (e) and (f) the EDS patterns of areas marked by +1 and +2 in (c).
The SEM micrographs of the samples sintered at different temperatures for 3 h are shown in Fig. 3. The morphology of the powder obtained at the low temperature showed that these products retained the characteristic of some fragments of the starting quartz (Fig. 3(a)). A mass of relatively well-developed and interlocked fibrous β-SiC grains are shown in Fig. 3(b), with an aspect ratio of >10 (0.05–0.3 mm in diameter). At temperatures above 1580 °C, the micro-morphologies of the powders were completely different. Fig. 3(c) shows that the products consisted of bulk materials and short columnar or granular agglomerates. The SEM micrograph and EDS results show that the short columnar or granular agglomerates were composed of β-Si₃N₄ particles, and the bulk materials were β-SiC grains (Fig. 3(e) and (f)). The well-developed β-Si₃N₄ grains with hexagonal rod-like shape can be seen in Fig. 3(d), with a diameter of 0.1–0.5 μm and a length of several micrometers.

Fig. 4 shows the TEM images and the XRD pattern of sample T2. The EDS spectrum and XRD pattern of sample T2 are shown in Fig. 4(c) and

Fig. 5. XRD patterns of samples S1-S4 sintered at different temperatures for 3 h: (a) 1580 °C; and (b) 1600 °C.
It can be seen that the main phase of the product of sample T2 was \(\beta\)-Si\(_3\)N\(_4\). We also observed the morphology of the synthesized \(\beta\)-Si\(_3\)N\(_4\) grain by TEM. Fig. 4(a) shows the typical TEM image of \(\beta\)-Si\(_3\)N\(_4\) grain. It can be seen that \(\beta\)-Si\(_3\)N\(_4\) grain had a well-developed rod-like structure, which was proved by the HRTEM image of \(\beta\)-Si\(_3\)N\(_4\) grain as shown in Fig. 4(b).

3.3. Influence of the C/SiO\(_2\) molar ratio on phase composition and micro-morphology of products

In this section, we discuss the influence of different C/SiO\(_2\) molar ratios on phase composition and micro-morphology of products. The XRD patterns of the samples with various C/SiO\(_2\) molar ratios sintered at 1580 °C and 1600 °C are shown in Fig. 5. It is shown clearly that the amount of \(\beta\)-SiC increased with the increase of the C/SiO\(_2\) molar ratio, while that of \(\beta\)-Si\(_3\)N\(_4\) dropped. When the C/SiO\(_2\) molar ratio is 3.0, \(\beta\)-SiC became the predominant crystalline phase. Besides, unreacted carbon could be found in the products of sample S4 sintered at 1600 °C (Fig. 5(b)). It is inferred that the excessive carbon promoted the formation reaction of \(\beta\)-SiC according to reaction (5) and the transformation process from \(\beta\)-Si\(_3\)N\(_4\) to \(\beta\)-SiC. Therefore, the optimum C/SiO\(_2\) molar ratio for the synthesis of \(\beta\)-Si\(_3\)N\(_4\) powder is 2.0, and the excessive carbon caused \(\beta\)-SiC forming in products.

Fig. 6 shows the SEM micrographs of the samples S1 and S4 sintered at 1600 °C for 3 h. It can be seen that the products of samples S1 and S4 demonstrated the particles of two different morphologies. Fig. 6(a) shows \(\beta\)-Si\(_3\)N\(_4\) grains presented a short hexagonal, rod-like morphology. The columnar \(\beta\)-SiC grains of 0.1–0.4 μm in diameter and 2–5 μm in length are shown in Fig. 6(b). It is deduced that the formation reaction of elongated or columnar \(\beta\)-SiC occurred mainly via reaction (5) or via the gas-phase reaction (10).

4. Conclusions

\(\beta\)-Si\(_3\)N\(_4\) powder has been successfully synthesized via the CRN process from quartz in flowing nitrogen atmosphere. C/SiO\(_2\) molar ratio of 2.0, amount of Fe\(_2\)O\(_3\) additive of 5.0 wt.%, temperature of 1600 °C and duration of 3 h are recommended. The prepared \(\beta\)-Si\(_3\)N\(_4\) grains present a short hexagonal, rod-like morphology, with a diameter of 0.1–0.5 μm and a length of several micrometers. Changes in experimental parameters including the reaction temperature, C/SiO\(_2\) molar ratio and amount of Fe\(_2\)O\(_3\) additive affect the phase compositions and the morphology of the products. \(\beta\)-Si\(_3\)N\(_4\) appeared in the products when the synthesis temperature was above 1580 °C. Excessive carbon promoted the formation reaction of \(\beta\)-SiC. Fe\(_2\)O\(_3\) additive exerted a significant promotion on the formation of \(\beta\)-Si\(_3\)N\(_4\) in CRN process by forming the low melting point eutectics, and 5.0 wt.% addition of Fe\(_2\)O\(_3\) was more favorable for the formation of \(\beta\)-Si\(_3\)N\(_4\).

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