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Synthesis of α-Si_3N_4 using low-α-phase Si_3N_4 diluent by the seeding technique

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An iterative method, called the seeding technique, was introduced into the traditional combustion synthesis process to synthesize α-Si_3N_4 powders, using low-α-phase Si_3N_4 diluent. The effect of the reaction thermodynamics and kinetics on the α-phase content of the synthesized product was discussed by calculating the conversion ratio of Si to α-Si_3N_4. The optimal conditions to obtain α-Si_3N_4 through the seeding technique have been determined.

Keywords: Seeding technique; Si_3N_4; The conversion ratio of Si to α-Si_3N_4; Self-propagating high-temperature synthesis (SHS); X-ray diffraction (XRD)

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) has proven advantages: lower energy requirement, higher product purity, simpler and cheaper equipment, and higher production rate [1]. It is well known that Si_3N_4 powders can be successfully obtained using SHS [2–4]. However, in order to improve the process and avoid incomplete nitridation, which can be a consequence higher reaction temperatures and rates, Si_3N_4 powders as diluent and ammonium salts as catalyst were added to the initial mixture. The incorporation of diluent and catalyst into the raw materials mixture affects which phase forms, as well as the phase composition of the synthesized product. Therefore, many studies have focused on the effect of the species and the amount of the diluent or catalyst added on the α-phase content of the synthesized product [5–8].

In our previous study, Si_3N_4 powders have been successfully obtained using SHS [9], and many SHS experiments have been carried out under the same process conditions of nitrogen pressure and amount of the diluent and catalyst added. It has been observed that the α-Si_3N_4 and β-Si_3N_4 phase proportion of the Si_3N_4 diluent strongly influenced the α-phase contents of the CS products. The point of this study was to investigate the effect of the α-phase content of the Si_3N_4 diluent on the α-phase content of the CS product, and to see how reaction thermodynamics and kinetics affect the α-phase content of the synthesized product in the iterative seeding process. Based on the research, high-α-Si_3N_4 powders have been synthesized by the seeding technique. The seeding was based on an iterative method, and consists of using the product of previous reactions as the Si_3N_4 diluent, and adding low-α-Si_3N_4 powders as diluent in the first step.

Silicon powders were used as reactant. The average grain size of silicon powder is 50 μm and their purity is higher than 99 wt.%. Si_3N_4 powder was added as diluent, and ammonium halides (NH_4Cl or NH_4F) were added as catalytic agents.

This process involves the following steps. Silicon, Si_3N_4 powder and ammonium halides (NH_4X) were mixed at the desired proportions and thoroughly ball-milled using steel balls with a ball:powder weight ratio of 10:1. The milled mixtures were then loosely loaded into a porous graphite crucible 350 mm in length, 80 mm wide and 45 mm high. The obtained charge of 400 g per batch was placed into a high-pressure vessel. After the reactor had been evacuated and then backfilled with nitrogen to ~3–5 MPa, the reactant mixture was ignited and the combustion reaction occurred. Different reaction parameters, including the composition of the starting powder mixture and the α-phase content of the Si_3N_4-diluent, were employed.

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The α-phase contents of the CS products were analyzed by X-ray diffraction (XRD) and calculated according to Gazzara and Messier [10]. Assuming that the α-Si_3N_4 and β-Si_3N_4 phase proportion of the Si_3N_4 diluent was unchanged throughout the reaction, that is to say, conversion of α-Si_3N_4 to β-Si_3N_4 in the Si_3N_4 diluent had not occurred, the conversion ratios of Si to α-Si_3N_4 expressed as $\eta_{Si\to\alpha}$ were calculated according to the α-phase contents of the combustion synthesized products of each synthesis. The α-phase content of the Si_3N_4 diluent and the α-phase content of the CS Si_3N_4 powders are named hereafter as α-dil and α-pro.

In order to investigate the effect of the α-dil on the α-pro, seven combustion reactions, E1–E7, were carried out by means of the seeding technique. In these reactions, the composition of the reactant mixture was $Si/Si_3N_4/NH_4Cl = 46.25/46.25/7.5$ (weight ratio) and the process conditions were kept the same. Figure 1(a) and (b) shows the XRD patterns of the products synthesized in E1–E7. The α-pro and the $\eta_{Si\to\alpha}$ of E1–E7 were calculated and are listed in Table 1. The α-phase content of the Si_3N_4 diluent used in E1 was 44.0 wt.%.

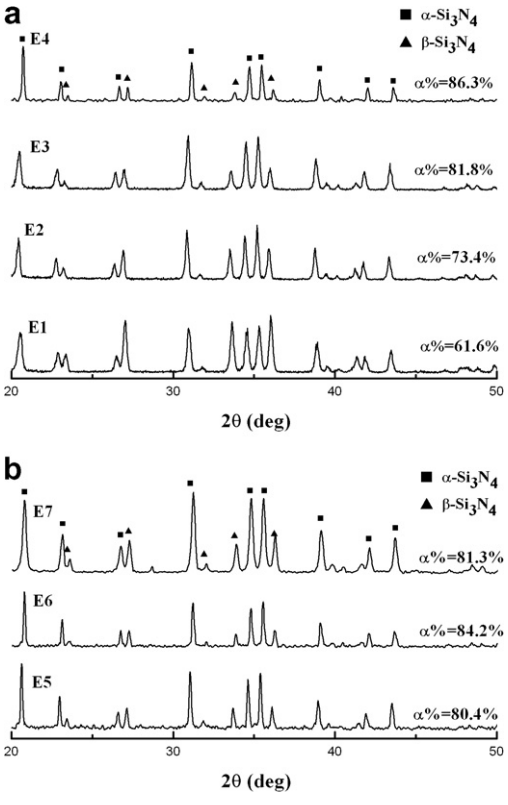

Figure 1. XRD patterns of the products synthesized in experiments E1–E7.

According to the XRD analysis results, shown in Figure 1(a) and (b), the products obtained in E1–E7 were only α-Si_3N_4 and β-Si_3N_4, and no residual Si could be detected, which means the complete nitridation of silicon was achieved in all experiments E1–E7. The influence of the α-dil on the α-pro can be seen from Table 1. In the current system, when the α-dil was lower than 86.3%, with the increase of the α-dil, the α-pro were considerably increased, and the $\eta_{Si\to\alpha}$ showed a similar trend, from 72.1% to 89.0%. However, when the α-dil reached a higher value, both the α-pro and $\eta_{Si\to\alpha}$ decreased, as shown in E5 and E7.

The reaction of nitridation of silicon can be represented as:

$$3(1-x)Si + 2(1-x)N_2 + xSi_3N_4 \rightarrow Si_3N_4.$$

The thermodynamic factor dQ_{Ex}/dm represents the heat per unit released from the reaction system. In this iterative seeding process, the value of dQ_{Ex}/dm for each Si_3N_4 CS process determined by the composition of the reactant mixture was the same. Based on the heterogeneous nucleation mechanism for the formation of Si_3N_4, a higher α-dil in the reactant mixture resulted in a lower activation energy for the formation of α-Si_3N_4, which increased the combustion wave velocity and the heat per second released from the reaction system, which is expressed as dQ_{Ex}/dt. Such rapid heat release lead to an increase of combustion temperature in the reactant system. It has been reported that α-Si_3N_4 is usually synthesized at or below 1400 °C. Above this temperature, α-Si_3N_4 would be transformed to β-Si_3N_4 powders [11,12]. Therefore, with an increase in α-dil, the value of dQ_{Ex}/dt increases, and the combustion temperature of the reactant system increases up to a value that could result in the conversion of α-Si_3N_4 to β-Si_3N_4; as a result, the α-pro certainly decreases. Such a explanation can be applied to the result above, for the $Si/Si_3N_4/NH_4Cl = 46.25/46.25/7.5$ system; both the α-pro and $\eta_{Si\to\alpha}$ decrease when the α-dil increases.

Figure 2(a)–(c) shows the first derivation of the temperature profile of the CS reaction in E1, E3 and E4, respectively. It can clearly be seen that the maximum value of the rate of temperature increase dT/dt is 13.3 in E1, 18.0 in E3 and 21.8 in E4. Correspondingly, the α-dil of the E1, E3 and E4 reactant systems increased gradually. Therefore, it can be deduced that the rise of dT/dt signifying the increase in dQ_{Ex}/dt can be attributed to the increase in the α-dil in the reactant mixture.

In summary, the thermodynamic factor dQ_{Ex}/dm and the kinetic factor dQ_{Ex}/dt simultaneously influence the α-phase content of the synthesized product. At lower α-dil, the effect of dQ_{Ex}/dm is dominant, and the value of dQ_{Ex}/dm depends on the composition of the reactant mixture affecting the $\eta_{Si\to\alpha}$ and its increment in each iterative CS reaction. However, with as α-dil increases, the

Table 1. The data of reactions in experiments E1–E7

Experiment	E1 %	E2 %	E3 %	E4 %	E5 %	E6 %	E7 %
α-Phase content of the Si_3N_4 diluent (α-dil)	44	61.6	73.4	81.8	86.3	80.4	84.2
α-Phase content of the synthesized Si_3N_4 powders (α-pro)	61.6	73.4	81.8	86.3	80.4	84.2	81.5
Conversion ratio of Si to α-Si_3N_4 ($\eta_{Si\to\alpha}$)	72.1	80.5	86.8	89.0	76.9	86.5	80.0